

Argonne National Laboratory

PICTORIAL STUDIES OF MOLECULES

I. Molecular Orbital Density Comparisons of H_2 , Li_2 , B_2 , C_2 , N_2 , O_2 , and F_2

by

Arnold C. Wahl

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ARGONNE NATIONAL LABORATORY
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Chemistry Division

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ABSTRACT

Contour diagrams of the molecular orbital and total electron densities of the homonuclear diatomic molecules H_2 , Li_2 , B_2 , C_2 , N_2 , O_2 , and F_2 are presented on a consistent basis convenient for comparison. These diagrams are calculated and drawn automatically by programs written by the author for the CDC-3600 computer. The molecular orbitals used in this study are the result of recent self-consistent field calculations and are thought to be very near the Hartree-Fock orbitals. The importance of such visual presentations is stressed, and further use in studies of chemical bond formation and molecular ionization indicated.

INTRODUCTION

For many years, physicists and chemists have been attempting to construct an adequate model of molecular structure. The major difficulty in constructing such a model within a rigorous mathematical framework arises from the currently intractable, multidimensional differential equations which quantum mechanics demands as the proper description of such systems of electrons and nuclei.

One of the most fruitful approaches to this problem was introduced in 1932 by R. S. Mulliken. In a now classic paper,¹ he developed for molecules the orbital theory, or "shell model," which had proven so useful in molecular spectroscopy and also as a working intuitive set of symbols for quantum chemists. The essence of the theory is that electrons occupy distinct orbitals, which may be characterized by a set of space and spin quantum numbers, and from which the total molecule may be constructed.

Until recently, however, the quantitative accuracy of this orbital model was poor, and it found its greatest use as an interpretive tool. Today, due to the rapid development of large electronic computers and the

concurrent sophistication in their use, it has become possible to perform the tremendous amount of algebra and arithmetic associated with the rigorous mathematical calculation of the exact properties of this shell model for diatomic molecules.²⁻⁵ An important outcome of these calculations is that the model is now documented and its usefulness being demonstrated.⁶⁻¹³ However, if the advances and refinements of this model, which have been made possible by high-speed computers, are only to be described in complex mathematical language or in terms of vast undigestible (and often misleading) numerical tables, they will have limited value.

Further, it has been in their utility in the past as a general, qualitative symbol that such models of molecular structure have proven very useful in providing new concepts for both experimental and theoretical investigators.

The above considerations motivated the present computational task of displaying directly these calculated molecular orbital and total molecular densities. It is further hoped that this effort provides an example of the presentation of the output of computer computations in an obvious, compact, and provocative way, making a part of the rich rewards of these calculations more readily available to a wider, and therefore potentially more fertile, audience.

REVIEW OF THEORY

According to molecular orbital theory,¹ the electronic structure of, for example, the fluorine molecule (F_2) is written

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^4: 1\Sigma_g^+$$

which designates that there are two electrons in the $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, and $3\sigma_g$ shells and four electrons in the $1\pi_u$ and $1\pi_g$ shells, and $1\Sigma_g^+$ is the spectroscopic notation for the ground state of the F_2 molecule. The corresponding electron configurations of the molecules studied in this work are given in Table I.

Mathematically, the total N electron-wave function is put forth as an antisymmetrical product of MSO's (Molecular Spin Orbitals):^{2,5}

$$\chi_K^\mu = \phi_i^\mu(\kappa) \eta_K^\mu, \quad (1)$$

where the superscript μ stands for the space and spin coordinates of the μ^{th} electron, and the subscripts κ and i label the different MSO's and MO's (Molecular Orbitals), respectively. In the following discussion the superscript μ and subscript κ are dropped to simplify the presentation to the features necessary in this pictorial study of the molecular orbitals ϕ_i .

To find the molecular orbitals, the total energy of the molecule would be varied with respect to the form of the molecular orbitals and the minimum found. However, due to current mathematical obstacles, the most convenient method of finding the molecular orbitals ϕ_i is to expand them in terms of a set of suitable expansion functions χ_p ,

$$\phi_i = \sum_p C_{ip} \chi_p, \quad (2)$$

where the C_{ip} 's are determined by the variational procedure, customarily through the iterative SCF (self-consistent-field) process.^{2,4,5}

In practice, a very close approximation to the molecular orbitals can be obtained in this way. Recent calculations of this type, utilizing analysis and computer programs developed by the author,^{2,3} have resulted in the determination of the molecular orbitals for a large number of diatomic molecules in the form of Eq. (2). These functions,^{2,7-11} which are thought to be very close to the Hartree-Fock (i.e., the molecular orbitals demanded by theory) result, were used in the pictorial calculations presented in this report.

DENSITIES AND CONTOURS

At this point, in order to clarify the diagrams of the shell model, it is convenient to introduce two new indices λ and α , which indicate, respectively, the symmetry species and subspecies of the molecular orbitals ϕ_i . The electronic density $\rho_{i\lambda}$ associated with the $i\lambda^{\text{th}}$ molecular shell at a point \underline{r} in space is defined by

$$\rho_{i\lambda}(\underline{r}) = e^{-N_{i\lambda}d_{\lambda}^{-1}} \sum_{\alpha} \phi_{i\lambda\alpha}(\underline{r}) \phi_{i\lambda\alpha}^*(\underline{r}), \quad (3)$$

where we have now grouped the molecular orbitals $\phi_{i\lambda\alpha}$ according to their symmetry species λ and their subspecies α , and have defined the density of shell $i\lambda$, which contains $N_{i\lambda}$ electrons, in terms of the sum over the modulus squared of the d_{λ} degenerate molecular orbitals making up the shell. The total electron density $\rho(\underline{r})$ of the molecule is then given by

$$\rho(\underline{r}) = \sum_{\lambda} \sum_i \rho_{i\lambda}(\underline{r}) \quad (4)$$

and is thus the sum of the densities of all shells making up the molecule.

The density associated with one of the d_λ degenerate molecular orbitals $\phi_{i\lambda\alpha}$ making up shell $i\lambda$ is

$$\rho_{i\lambda\alpha}(\mathbf{r}) = \rho_{i\lambda}(\mathbf{r})/d_\lambda, \quad (5)$$

which is just the shell density divided by the number of degenerate molecular orbitals making up the shell. In the diagrams presented in this report, the total density [Eq. (4)] and the orbital density [Eq. (5)] have been plotted. (For σ symmetry, $d_\lambda = 1$, and thus the orbital density equals the shell density; for π symmetry in diatomic molecules, $d_\lambda = 2$, and the orbital density equals half of the shell density. The molecular shells and their occupation $N_{i\lambda}$ are given in Table I for the molecules studied. The only molecular symmetries occurring in this work are σ_g , σ_u , π_u , and π_g .¹⁾)

In what follows in this section, the symmetry indices λ and α of the orbital density $\rho_{i\lambda\alpha}(\mathbf{r})$ will be suppressed since they are unnecessary for the description of the contour drawing process.

An orbital contour line indicating a density C in the xz plane (ρ and ρ_i for diatomic molecules are cylindrically symmetric about the z axis, and plots in any plane containing this axis convey complete density information) may be defined by the equation,

$$\rho_i(x, z) = C,$$

and its path by the relation,

$$\frac{d\rho_i}{dx} \Delta x + \frac{d\rho_i}{dz} \Delta z = 0,$$

which gives the direction of the tangent to the contour at any point on it to be

$$\frac{\Delta x}{\Delta z} = - \frac{d\rho_i/dz}{d\rho_i/dx}. \quad (6)$$

A step $\Delta s = (\Delta x^2 + \Delta z^2)^{\frac{1}{2}}$ is taken along this tangent, and a density found such that

$$\rho_i'(x + \Delta x, z + \Delta z) = C + \Delta\rho_i. \quad (7)$$

Then a correction is applied perpendicular to initial tangent along the new line

$$\frac{\Delta x'}{\Delta z'} = + \frac{d\rho_i/dx}{d\rho_i/dz}$$

a distance

$$\Delta z' = \frac{\Delta \rho}{\left(\frac{d\rho'_1}{dz'} + \frac{d\rho'_1}{dx'} \frac{d\rho_1/dx}{d\rho_1/dz} \right)}. \quad (8)$$

This correction [Eq. (8)] is continued until $\Delta \rho$ falls within a small preset threshold. This hunt process [Eqs. (6-8)] is continued until the entire contour is traced out. Analogous equations result for the total molecular density or for any linear combination of molecular orbital densities.

THE COMPUTER PROGRAM

When the molecular orbitals are expanded in terms of a linear combination of symmetry expansion functions, the result is

$$\phi_{i\lambda\alpha} = \sum_p C_{ip\lambda} \chi_{p\lambda\alpha},$$

where, for convenience, the expansion functions possess the same symmetry as the molecular orbital.² Then Eqs. (4) and (5) become

$$\rho(\underline{r}) = e^{-\sum_{\lambda} \sum_i N_{i\lambda} \left| \sum_p C_{ip\lambda} \chi_{p\lambda\alpha}(\underline{r}) \right|^2}, \quad (9)$$

and

$$\rho_{i\lambda\alpha}(\underline{r}) = e^{-N_{i\lambda} d\lambda^1 \left| \sum_p C_{ip\lambda} \chi_{p\lambda\alpha}(\underline{r}) \right|^2}, \quad (10)$$

where, in going from Eqs. (4) and (5), the summation over α has been eliminated since it yields identical contributions. Again, dropping symmetry indices, Eq. (6) becomes

$$\frac{\Delta x}{\Delta z} = \frac{\left[\sum_{pq} C_{ip} C_{iq} \left(\chi_p \frac{d\chi_q}{dz} + \chi_q \frac{d\chi_p}{dz} \right) \right]}{\left[\sum_{pq} C_{ip} C_{iq} \left(\chi_p \frac{d\chi_q}{dx} + \chi_q \frac{d\chi_p}{dx} \right) \right]}. \quad (11)$$

In this study, the expansion functions χ_p used were the two center-symmetry Slater-type basis functions employed in SCF calculations described recently.² The derivatives of these functions can be evaluated in a straightforward fashion.

General automatic programs were constructed by the author for the CDC-3600 computer with an on-line DD 80 plotter (at Argonne National Laboratory), which automatically hunted and plotted a given set of contour values for a single or linear combination of molecular orbitals ϕ_i in the expansion form for either homonuclear or heteronuclear diatomic molecules. Using Eq. (10), a contour value was found and a contour line was hunted out by proceeding along the tangent [Eq. (11)] a small increment, and iterating perpendicular to the tangent (i.e., along the new line $\Delta x'/\Delta y' = -\Delta y/\Delta x$) until the contour value was relocated with 1%. By the repetition of this process, the entire contour was traced out. Straight-line segments were then plotted between adjacent points, thus yielding as computer time exposures the smooth-contour curves displayed in the figures. For the total density, Eq. (9) and its derivatives were used.

The input to the program consists of the symmetry basis functions $\chi_{p\lambda\alpha}$, the orbital coefficients $C_{ip\lambda}$,¹⁴ the internuclear distance R , a series of the contour values desired with the associated thresholds, and finally the physical scale in which diagrams are to be plotted. The output consisted of 35-mm negatives of the diagrams presented in this work.

RESULTS AND IMPLICATIONS

In Figs. 1-41, the contours of density associated with the homonuclear diatomic molecules constructed from first-row atoms are given on a consistent basis as defined in Table II. Both the total molecular densities and the orbital densities are displayed for each molecule at its experimental internuclear distance.

The concept of a shell may certainly be visualized in terms of these distributions of the electrons assigned to that shell. In the contour diagrams, the difference between shells is clear as the difference in the value of electronic density in corresponding regions of space and in the overall pattern of contours. The difference between the shell and total densities of the various molecules as displayed in Table III is also of interest.¹⁵

It is hoped that these contour diagrams of the shell model for these simple homonuclear diatomic molecules, H_2 , Li_2 , B_2 , C_2 , N_2 , O_2 , and F_2 , will prove to be useful symbols which will stimulate thought about chemical binding, steric hindrance, and bonding and antibonding orbitals, in addition to providing a correct, more complete, and quantitative picture

of the shell model where only a rudimentary one, based primarily on hydrogen atom wave functions, existed before.

In further use of these computational techniques, concepts and changes that are best presented visually may be so presented. Such visual presentations have been quite limited in the past due to the prohibitive labor involved.^{6,13} The completely automatic programs developed in this work make it easy to analyze visually a very large amount of calculated data. Studies of interatomic forces and the formation of the chemical bond are underway in which these programs are being used to display the changes occurring in electronic charge density as a molecule forms.¹⁶ In a study of molecular ionization, these automatic contour programs are being used to illustrate directly changes in the molecular charge distribution with electron removal.¹⁷ In other theoretical work, a pictorial display¹⁸ of configuration mixing also in progress provides a physical picture of wave-function improvements and electron correlation as produced by added optimal configurations.

In closing, it should be pointed out that this work represents primarily the development of a new tool, namely, the synthesis of programming skill, high-speed digital computers, and linked analog devices into a medium capable of efficiently communicating certain types of new information. Since many of us involved in large-scale computational efforts are often swamped by our own computer output and are able to analyze competently only a small fraction of the potentially useful information we have generated, this problem of communication is well worth consideration.

ACKNOWLEDGMENT

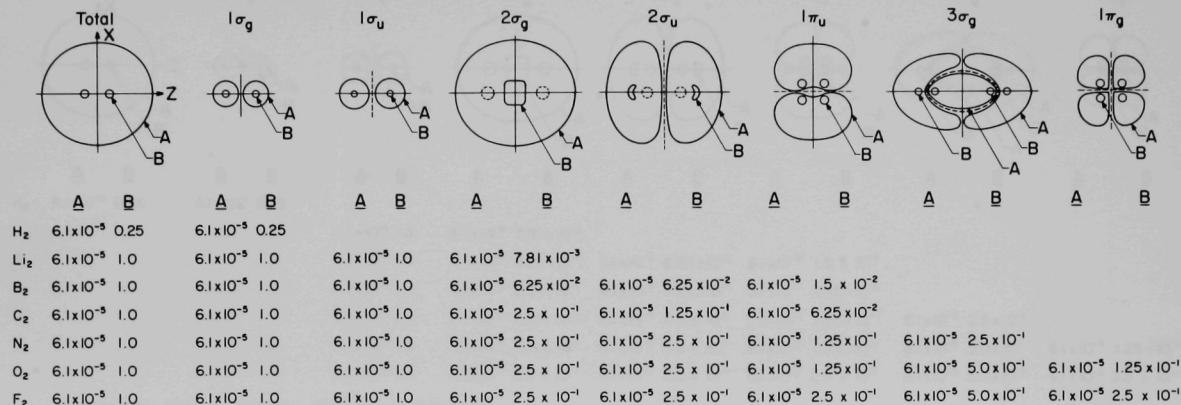
The author is particularly grateful to the Computation Center Staff of the CDC-3600 computer and the Applied Mathematics Division at Argonne National Laboratory for their painstaking efforts in processing these calculations, maintaining the DD 80 plotter, and providing library programs, all of which greatly facilitated the work presented in this paper.


TABLE I. Electron Configuration of Molecules

Total Molecular Density	Molecular Shells and Index to Contour Diagrams								Spectroscopic Designation
H ₂ (1)	1σ _g ² (2)								1Σ _g ⁺
He ₂	1σ _g ²	1σ _u ²							1Σ _g ⁺
Li ₂ (3)	1σ _g ² (4)	1σ _u ² (5)	2σ _g ² (6)						1Σ _g ⁺
Be ₂	1σ _g ²	1σ _u ²	2σ _g ²	2σ _u ²					1Σ _g ⁺
B ₂ (7)	1σ _g ² (8)	1σ _u ² (9)	2σ _g ² (10)	2σ _u ² (11)	1π _u ² (12)				3Σ _g ⁻
C ₂ (13)	1σ _g ² (14)	1σ _u ² (15)	2σ _g ² (16)	2σ _u ² (17)	1π _u ⁴ (18)				1Σ _g ⁺
N ₂ (19)	1σ _g ² (20)	1σ _u ² (21)	2σ _g ² (22)	2σ _u ² (23)	1π _u ⁴ (24)	3σ _g ² (25)			1Σ _g ⁺
O ₂ (26)	1σ _g ² (27)	1σ _u ² (28)	2σ _g ² (29)	2σ _u ² (30)	1π _u ⁴ (31)	3σ _g ² (32)	1π _g ² (33)		3Σ _g ⁻
F ₂ (34)	1σ _g ² (35)	1σ _u ² (36)	2σ _g ² (37)	2σ _u ² (38)	1π _u ⁴ (39)	3σ _g ² (40)	1π _g ⁴ (41)		1Σ _g ⁺
Ne ₂	1σ _g ²	1σ _u ²	2σ _g ²	2σ _u ²	1π _u ⁴	3σ _g ²	1π _g ⁴	3σ _u ²	1Σ _g ⁺

Superscript of 2 or 4 indicates number of electrons $N_{i\lambda}$ occupying molecular shell $i\lambda$. Number of diagram is in parentheses to right of symbol. For the π shells, which consist of two degenerate molecular orbitals, a molecular orbital, containing half of the electrons in the π shell, has been plotted.

TABLE II. Key to Density Contours in Figures 1-41



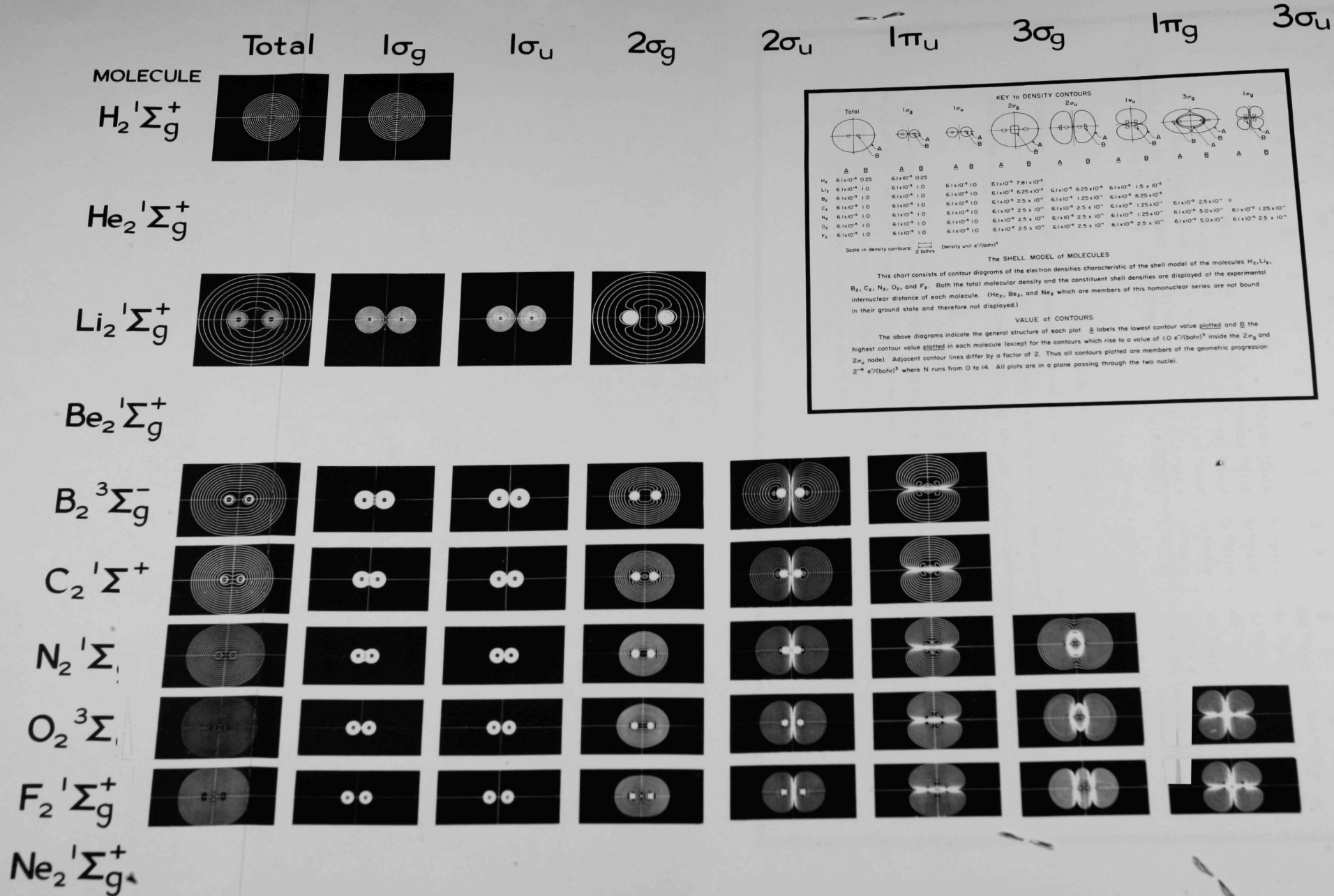
Diagrams 1-41:  Density unit $e^-/(\text{bohr})^3$

The SHELL MODEL of MOLECULES

Diagrams 1-41 are contour diagrams of the electron densities characteristic of the shell model of the molecules H_2 , Li_2 , B_2 , C_2 , N_2 , O_2 , and F_2 . Both the total molecular density and the constituent shell densities are displayed at the experimental internuclear distance of each molecule. (He_2 , Be_2 , and Ne_2 which are members of this homonuclear series are not bound in their ground state and therefore not displayed.)

VALUE of CONTOURS

The above diagrams indicate the general structure of each plot. A labels the lowest contour value plotted and B the highest contour value plotted in each molecule (except for the contours which rise to a value of $1.0 e^-/(\text{bohr})^3$ inside the $2\sigma_g$ and $2\sigma_u$ node). Adjacent contour lines differ by a factor of 2. Thus all contours plotted are members of the geometric progression $2^{-N} e^-/(\text{bohr})^3$ where N runs from 0 to 14. All plots are in a plane passing through the two nuclei. Dotted lines indicate nodal surface.



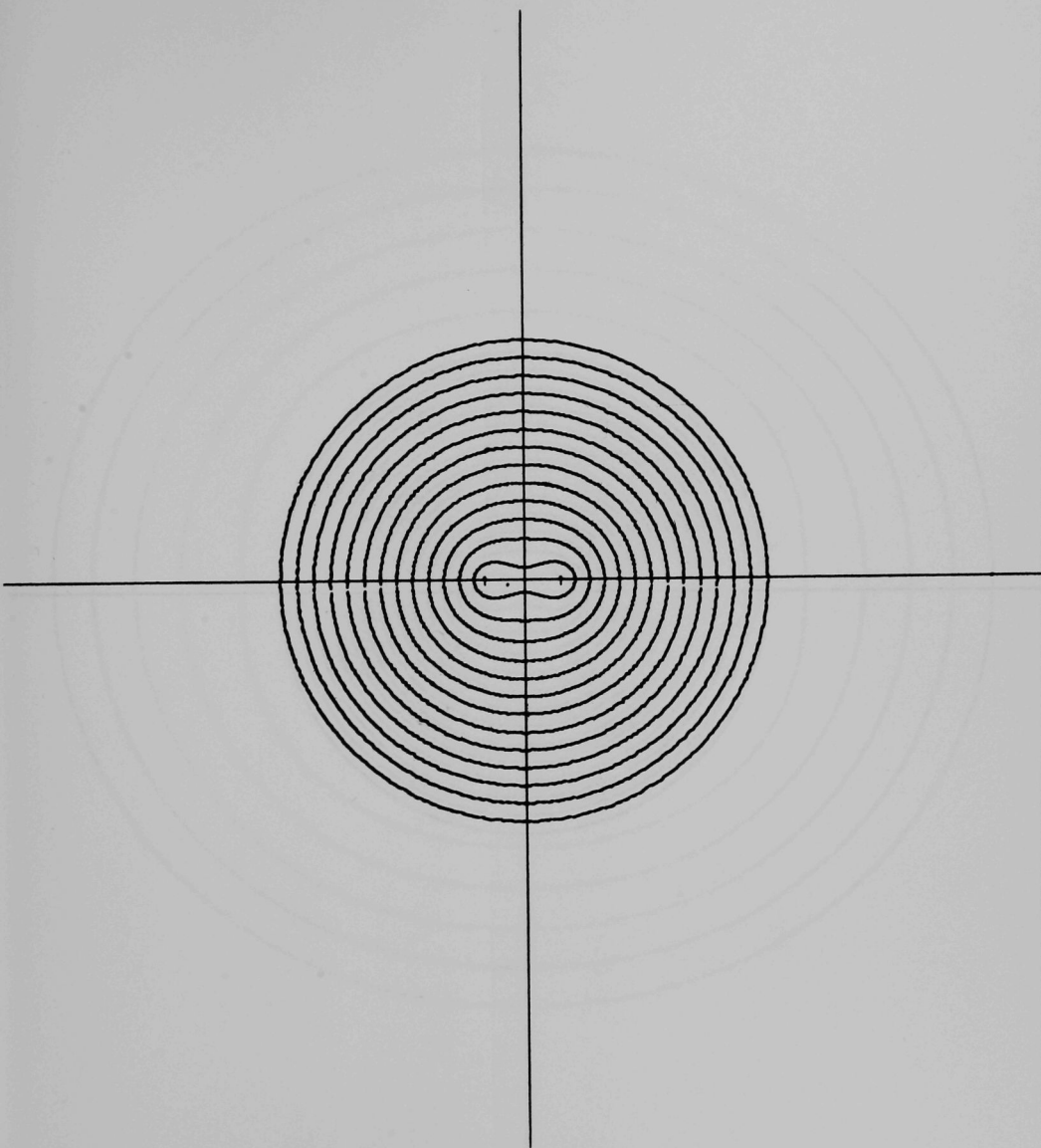


Fig. 1. Hydrogen Total Molecular Density

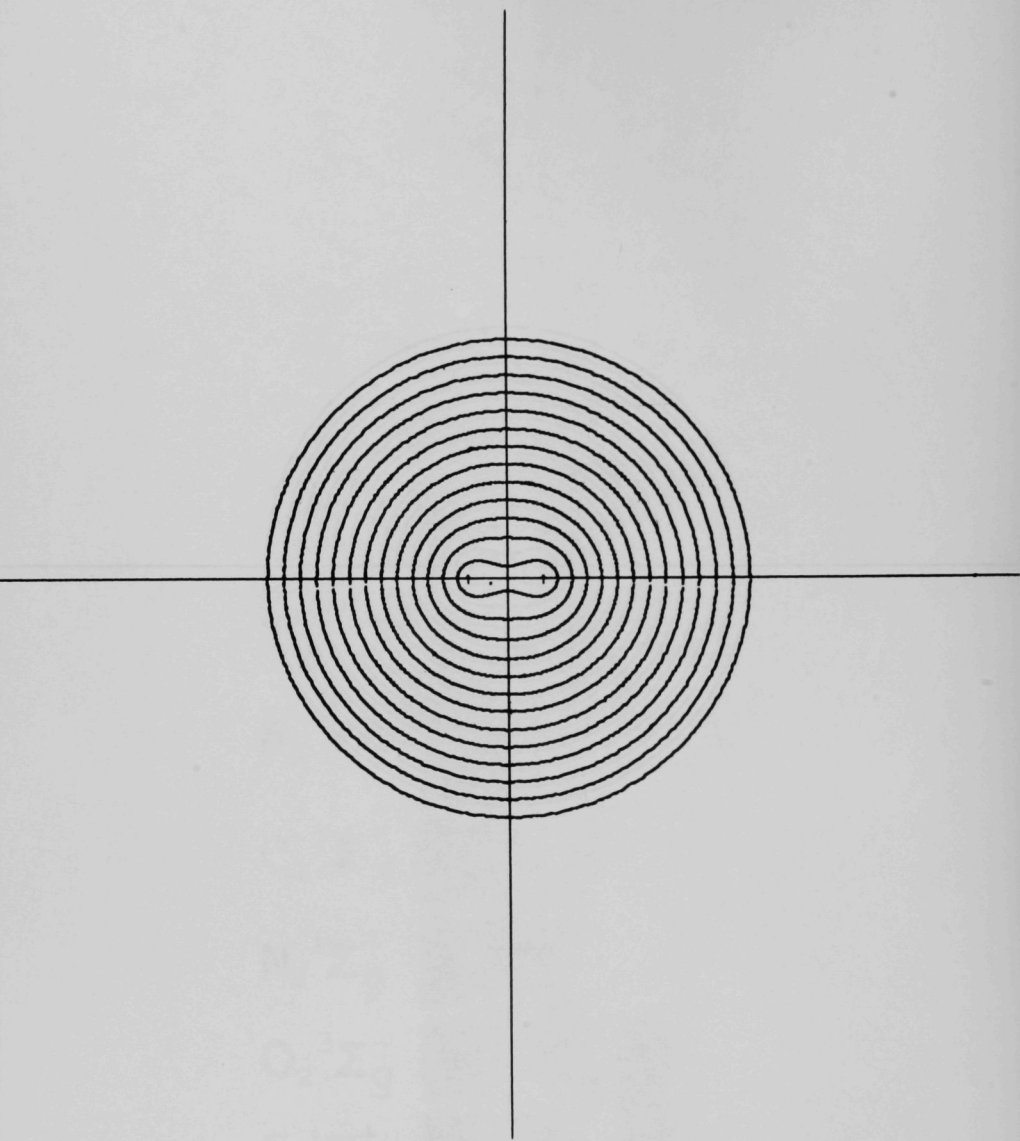


Fig. 2. Hydrogen $1\sigma_g$ Orbital Density

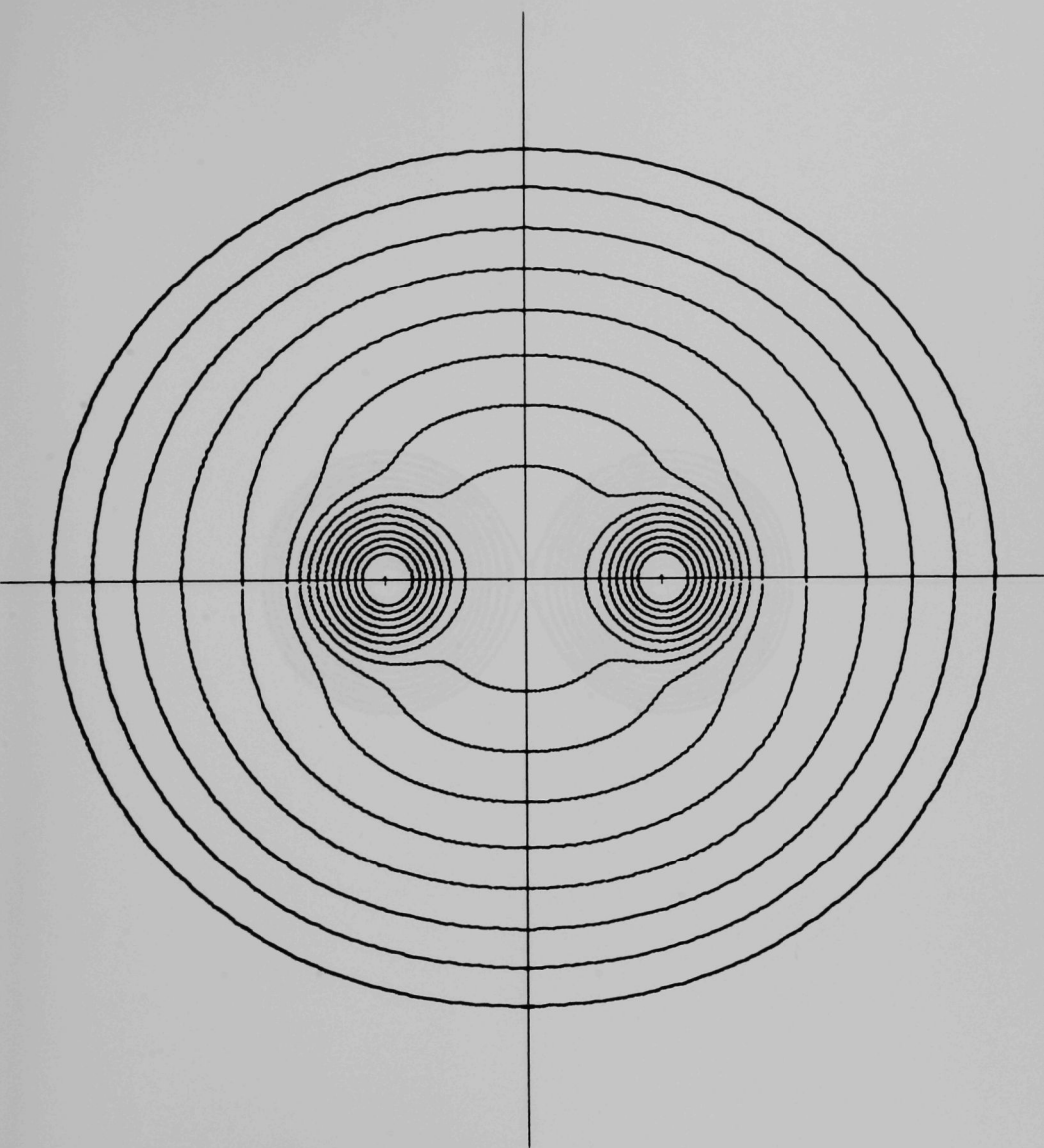


Fig. 3. Lithium Total Molecular Density

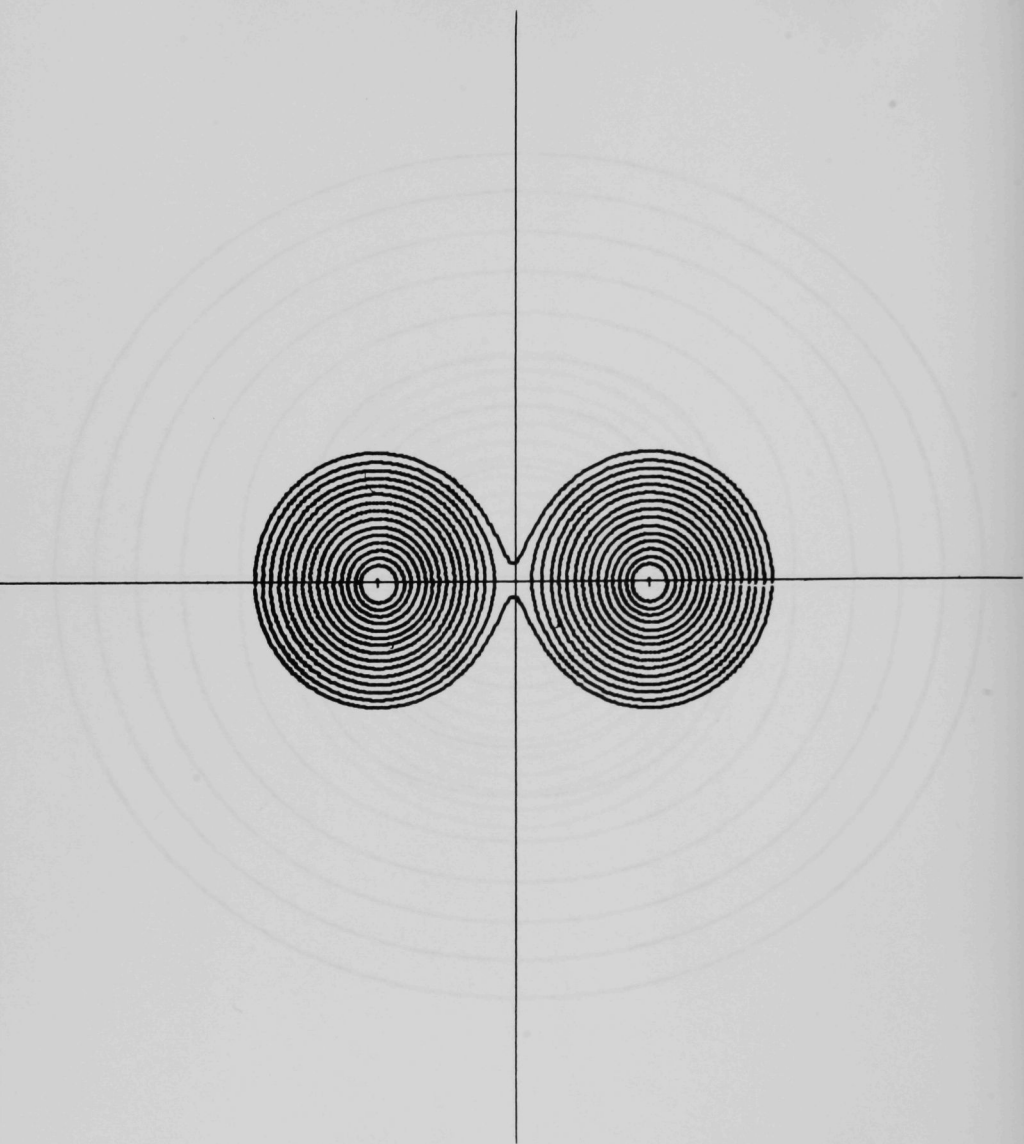


Fig. 4. Lithium $1\sigma_g$ Orbital Density

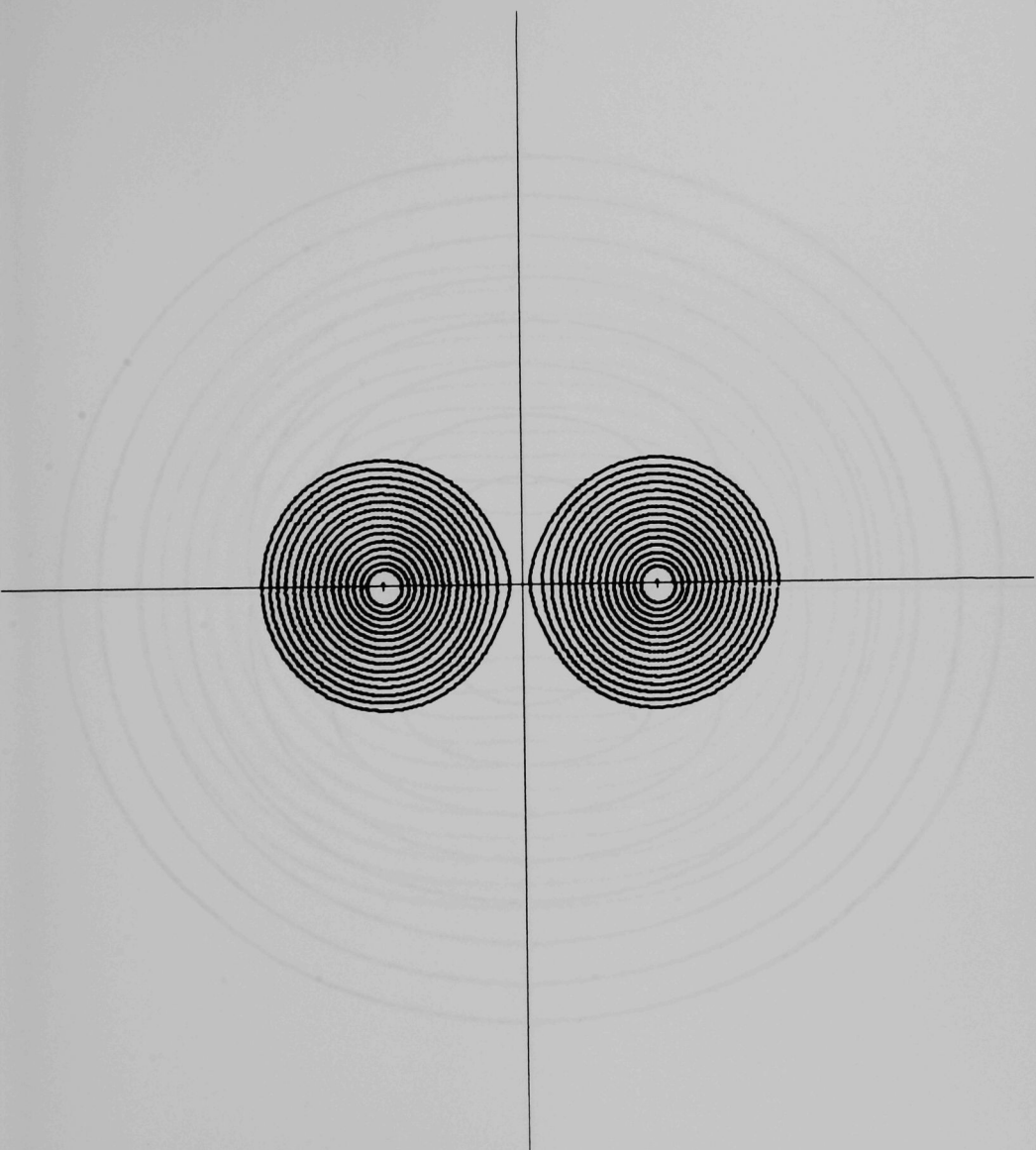


Fig. 5. Lithium $1\sigma_u$ Orbital Density

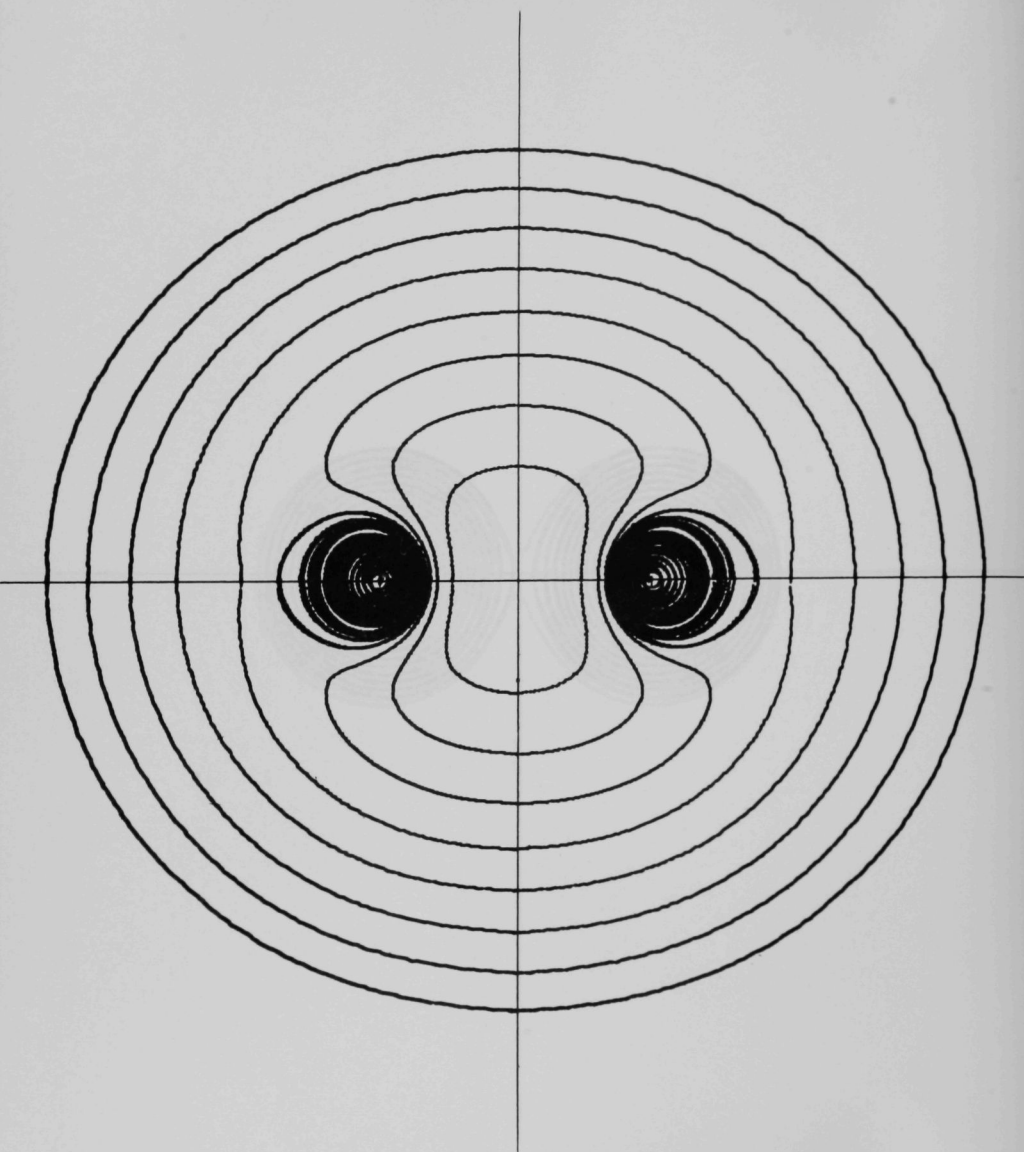


Fig. 6. Lithium $2\sigma_g^*$ Orbital Density

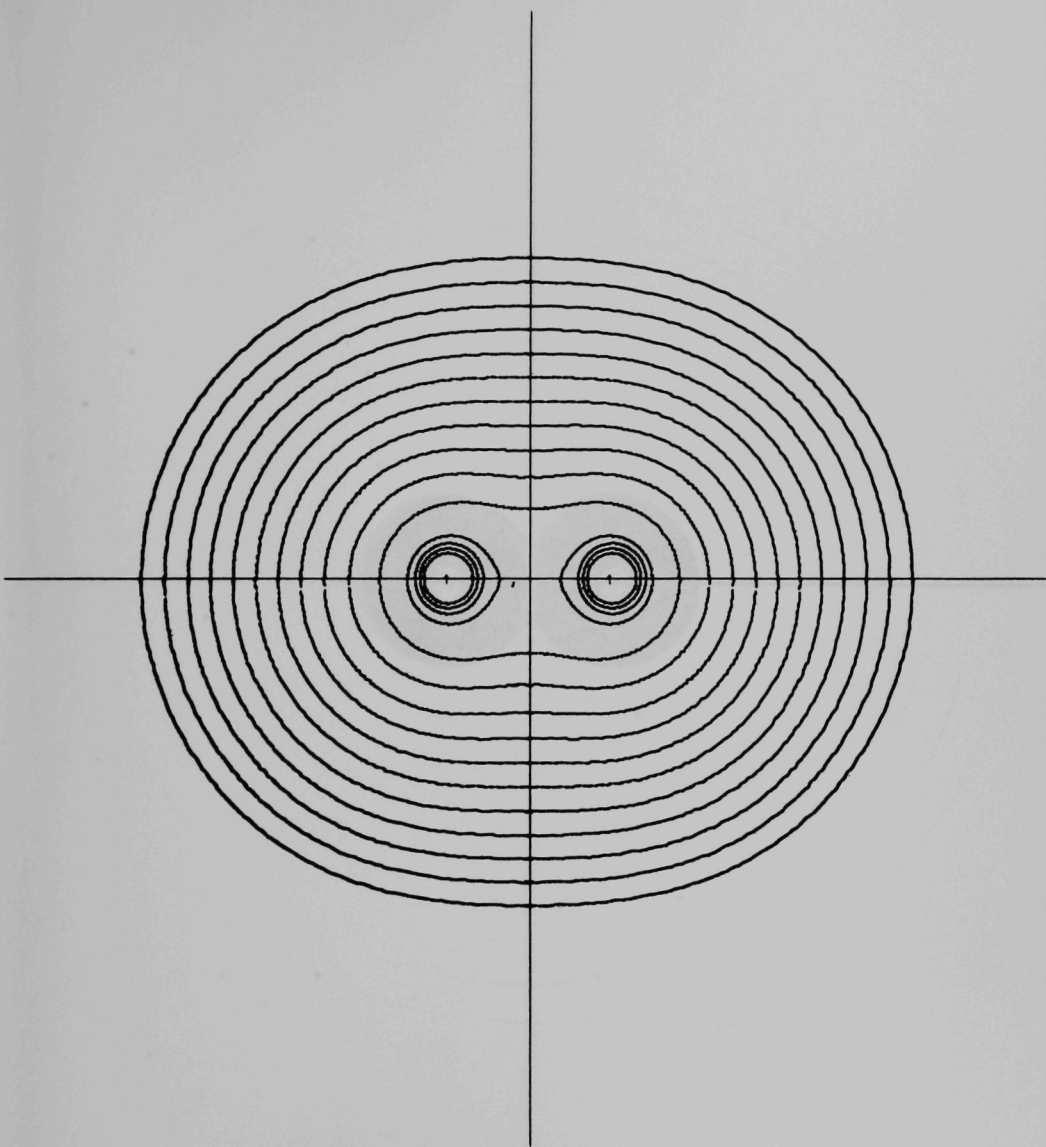


Fig. 7. Boron Total Molecular Density

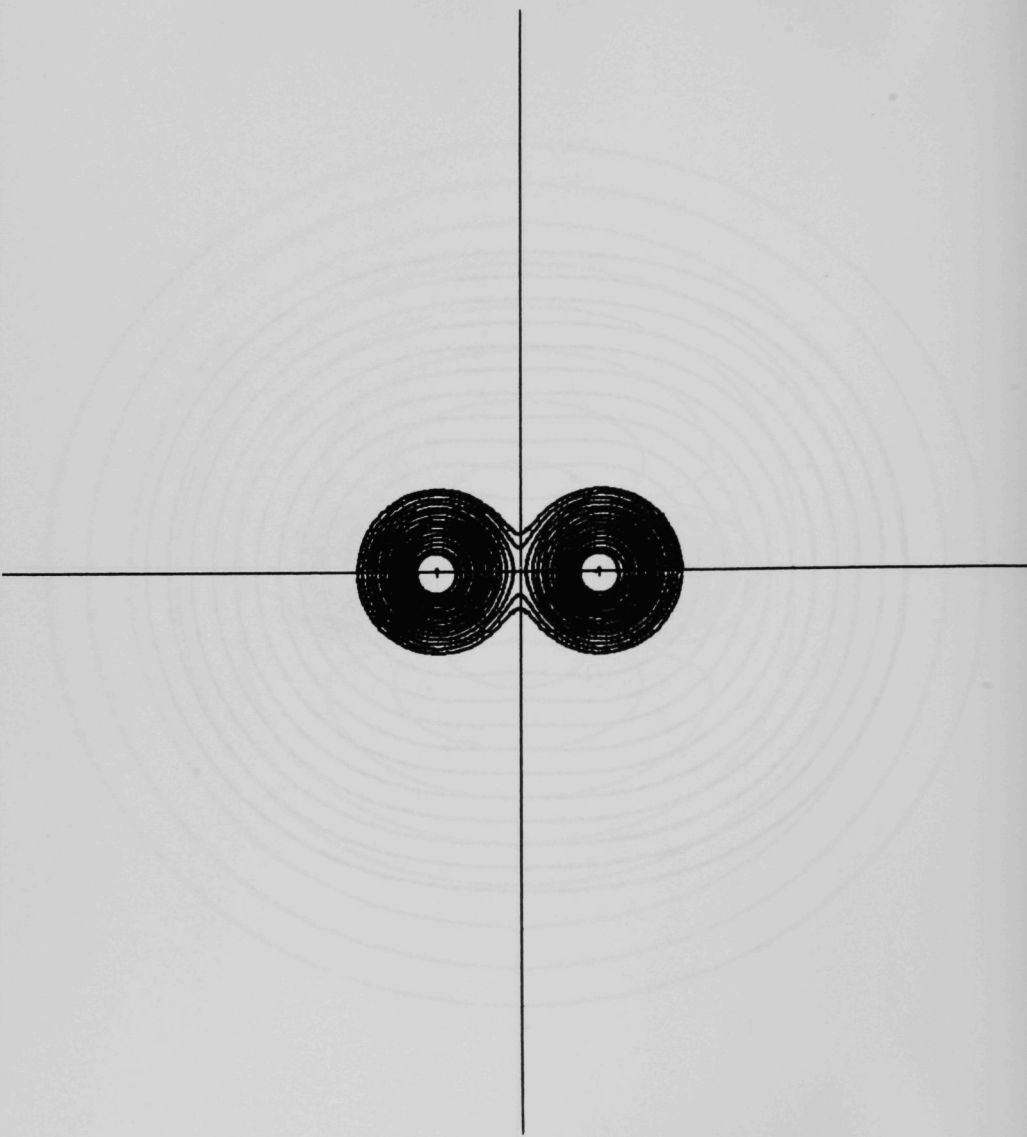


Fig. 8. Boron $1\sigma_g$ Orbital Density

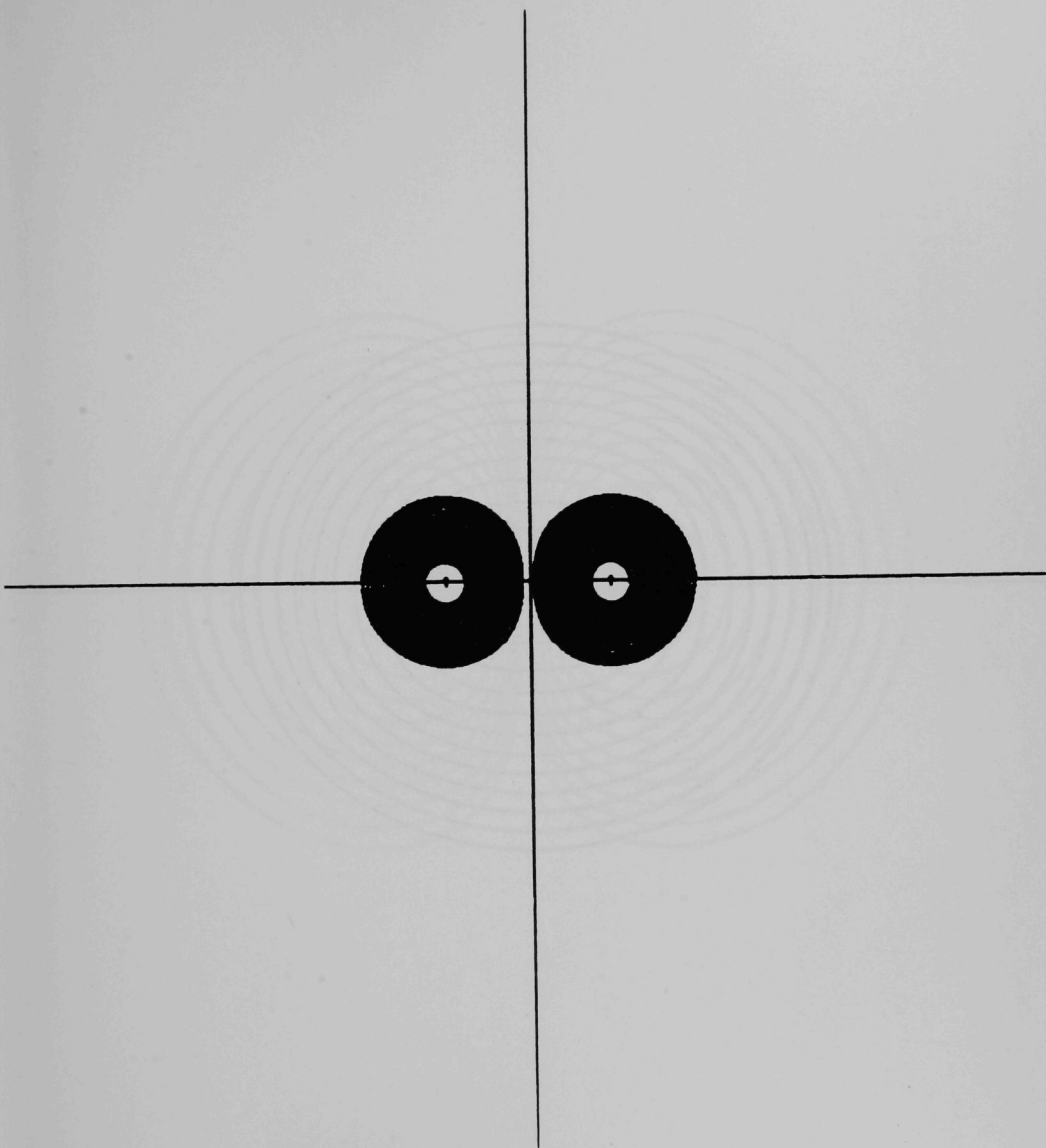


Fig. 9. Boron $1\sigma_u$ Orbital Density

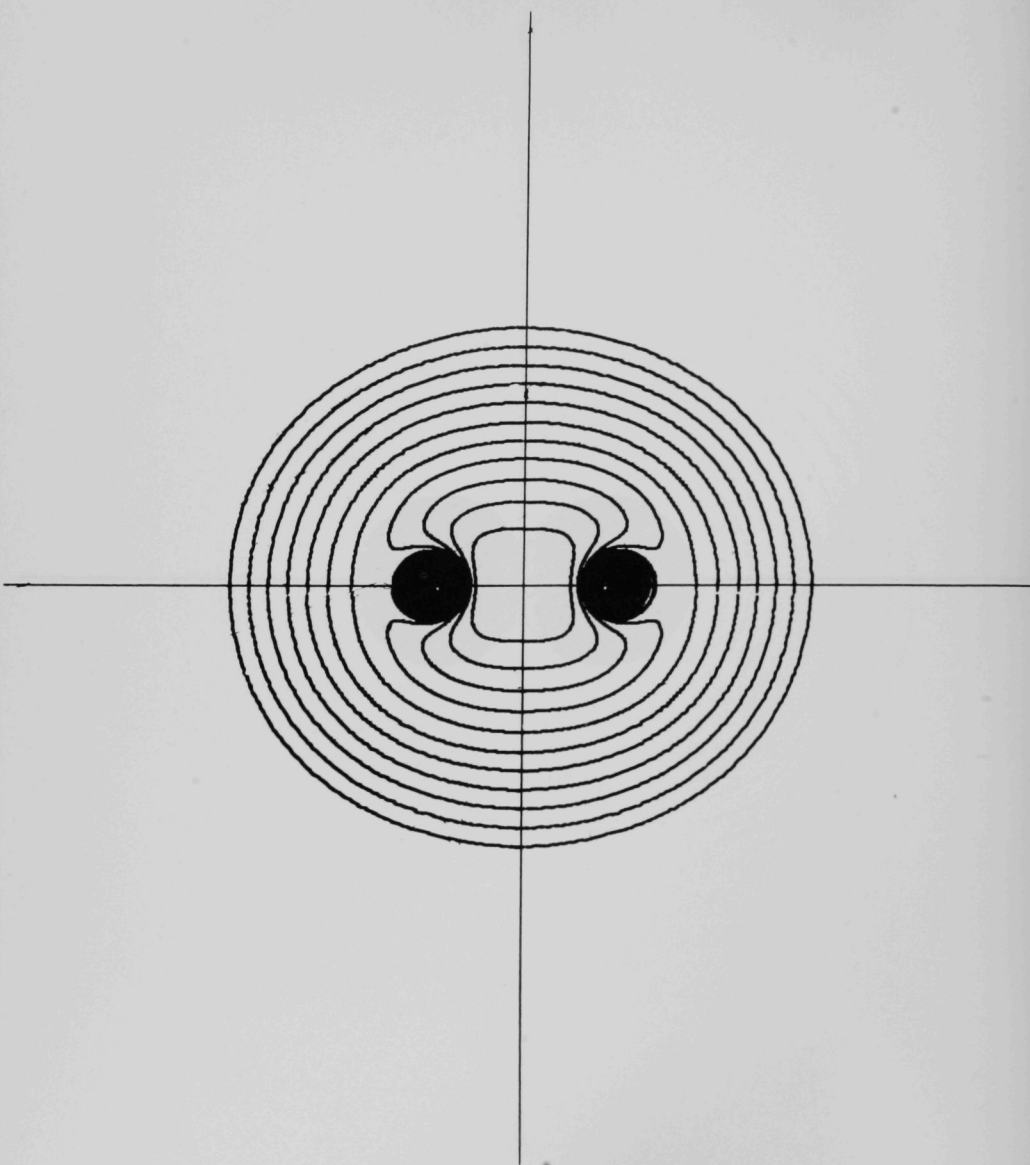


Fig. 10. Boron $2\sigma_g^*$ Orbital Density

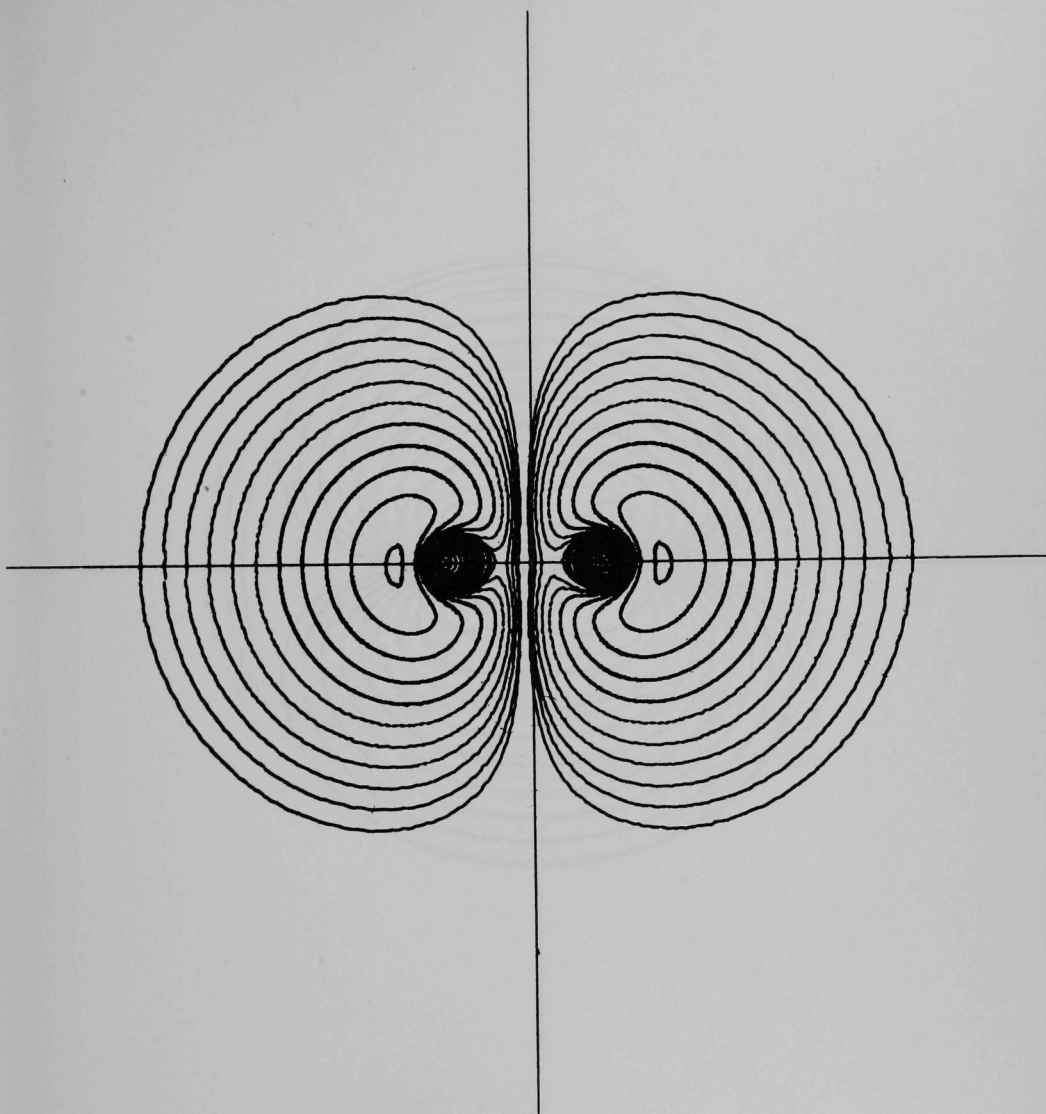


Fig. 11. Boron $2\sigma_u$ Orbital Density

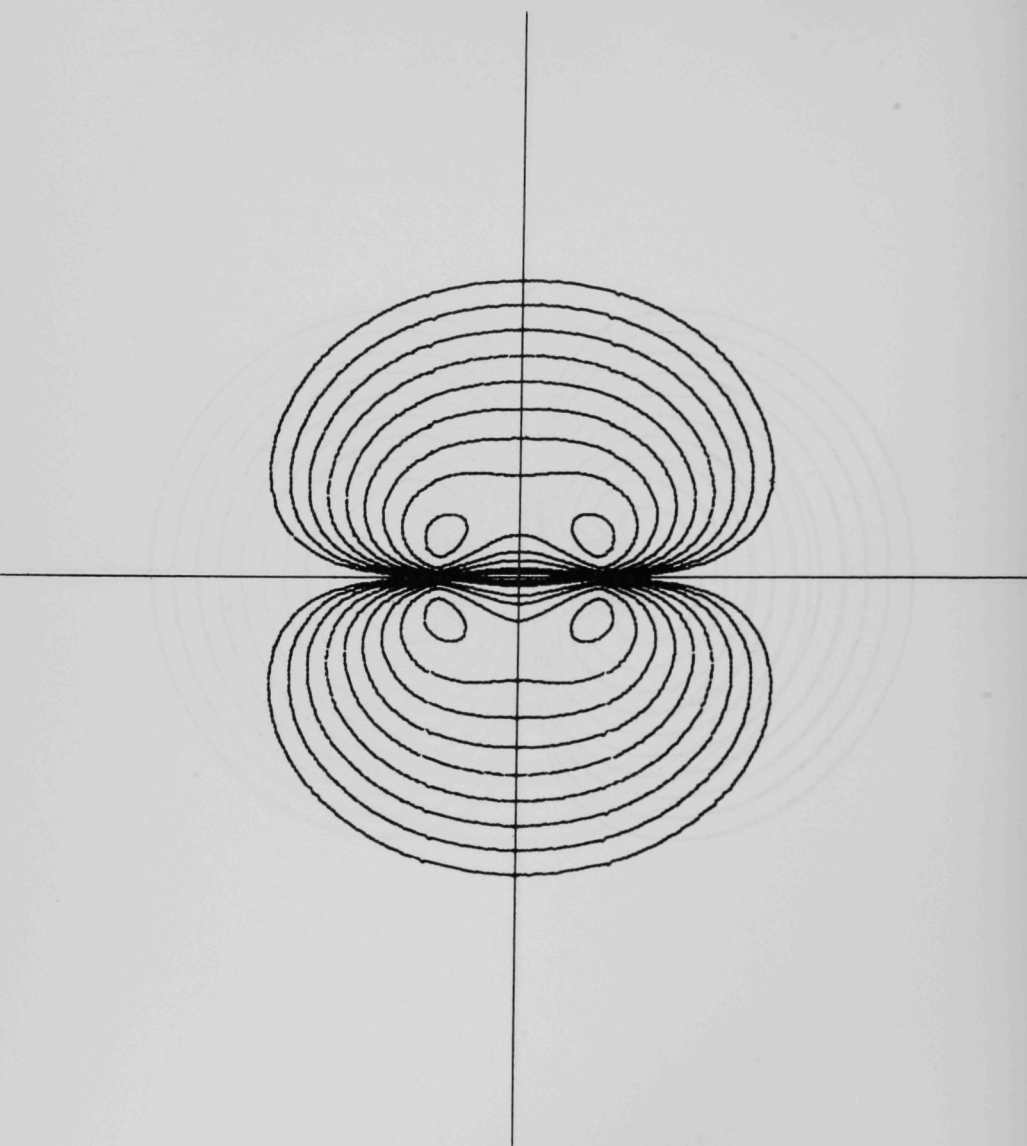


Fig. 12. Boron $1\pi_u$ Orbital Density

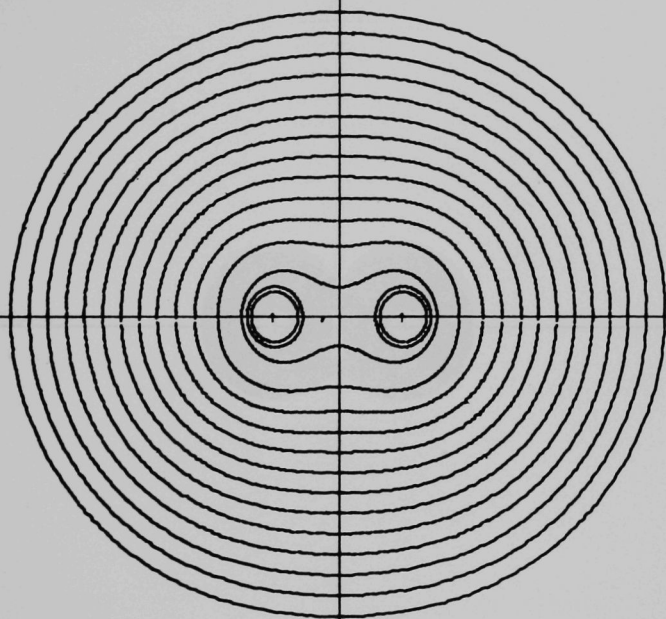


Fig. 13. Carbon Total Molecular Density

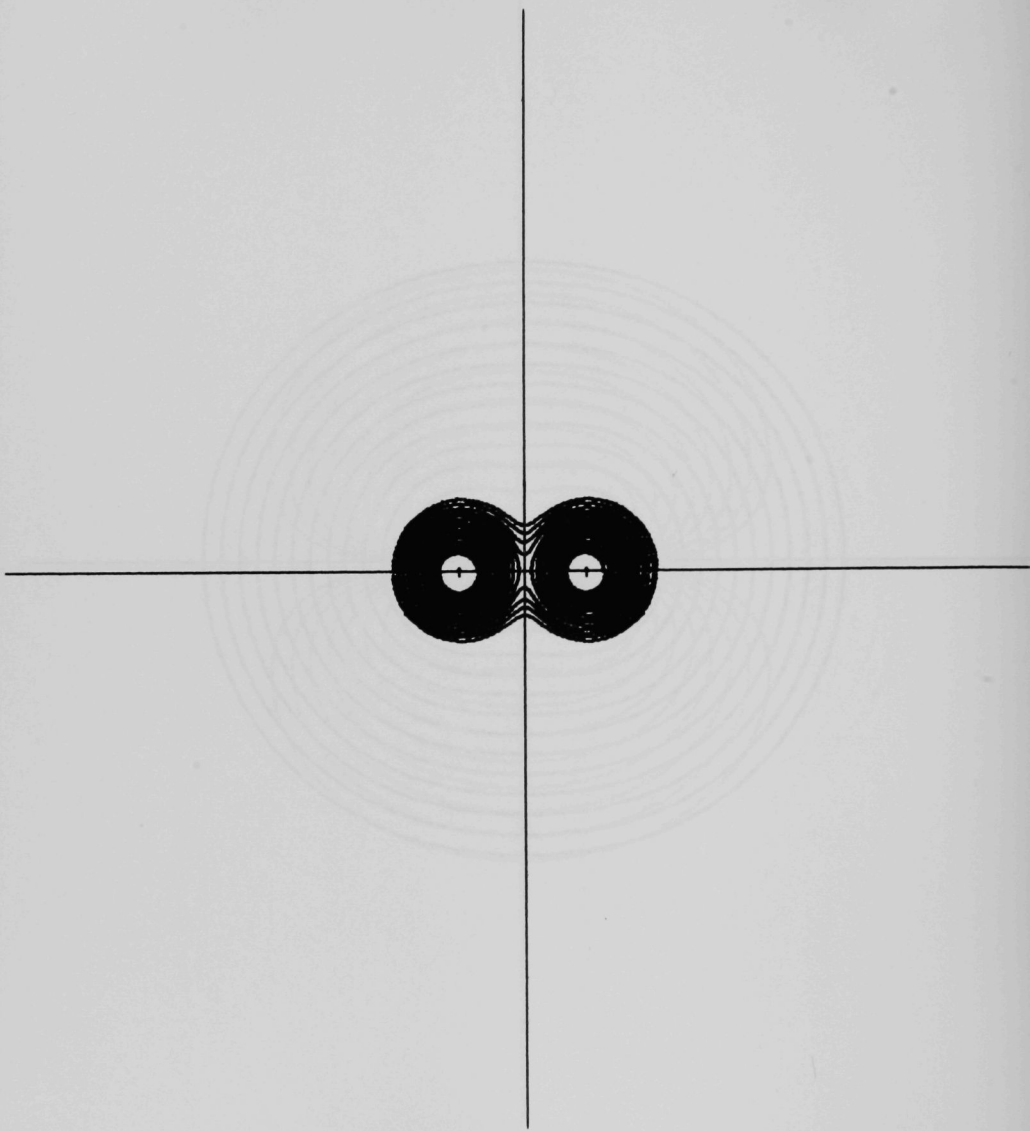


Fig. 14. Carbon $1\sigma_g^*$ Orbital Density

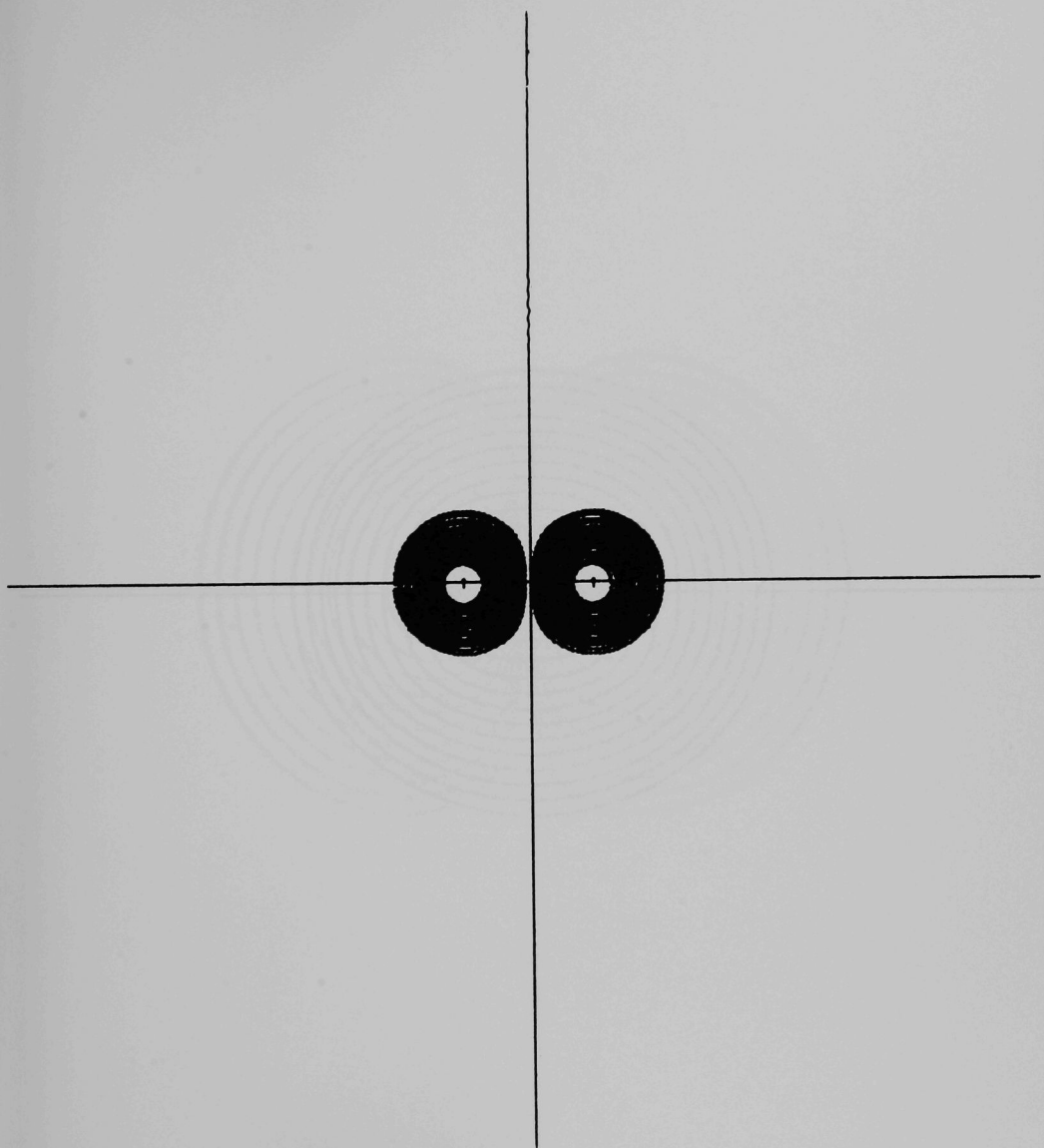


Fig. 15. Carbon $1\sigma_u$ Orbital Density

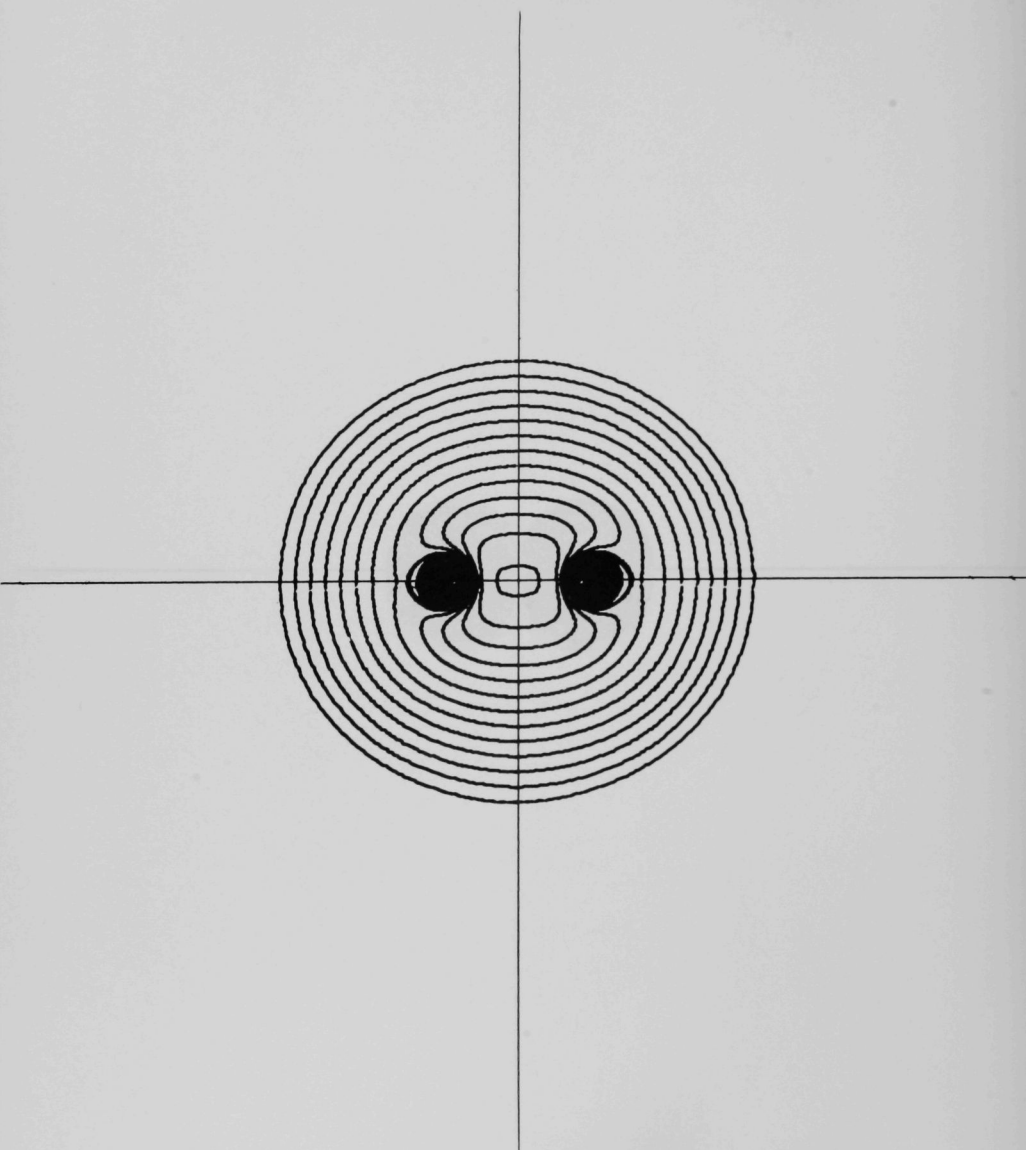


Fig. 16. Carbon $2\sigma_g^*$ Orbital Density

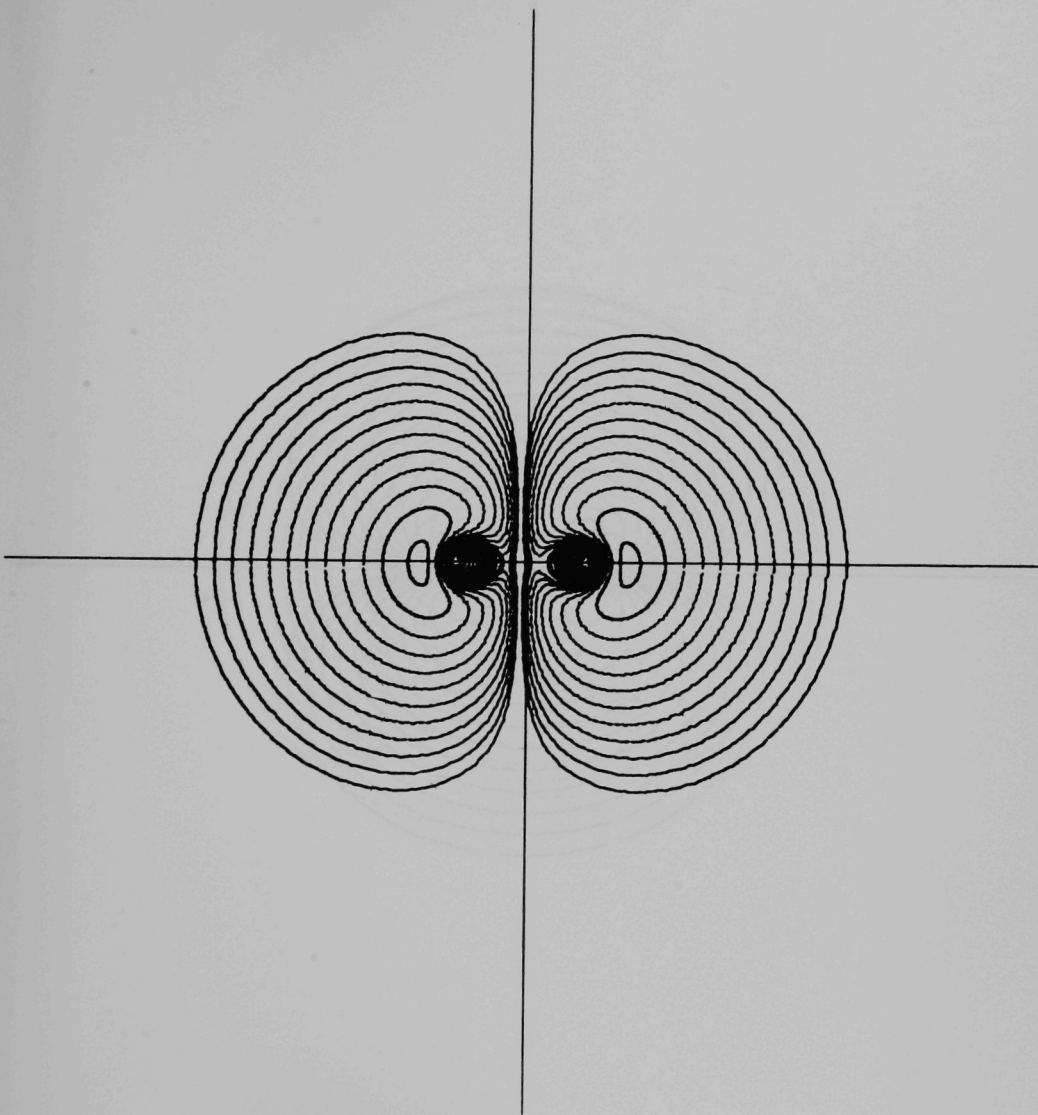


Fig. 17. Carbon $2\sigma_u$ Orbital Density

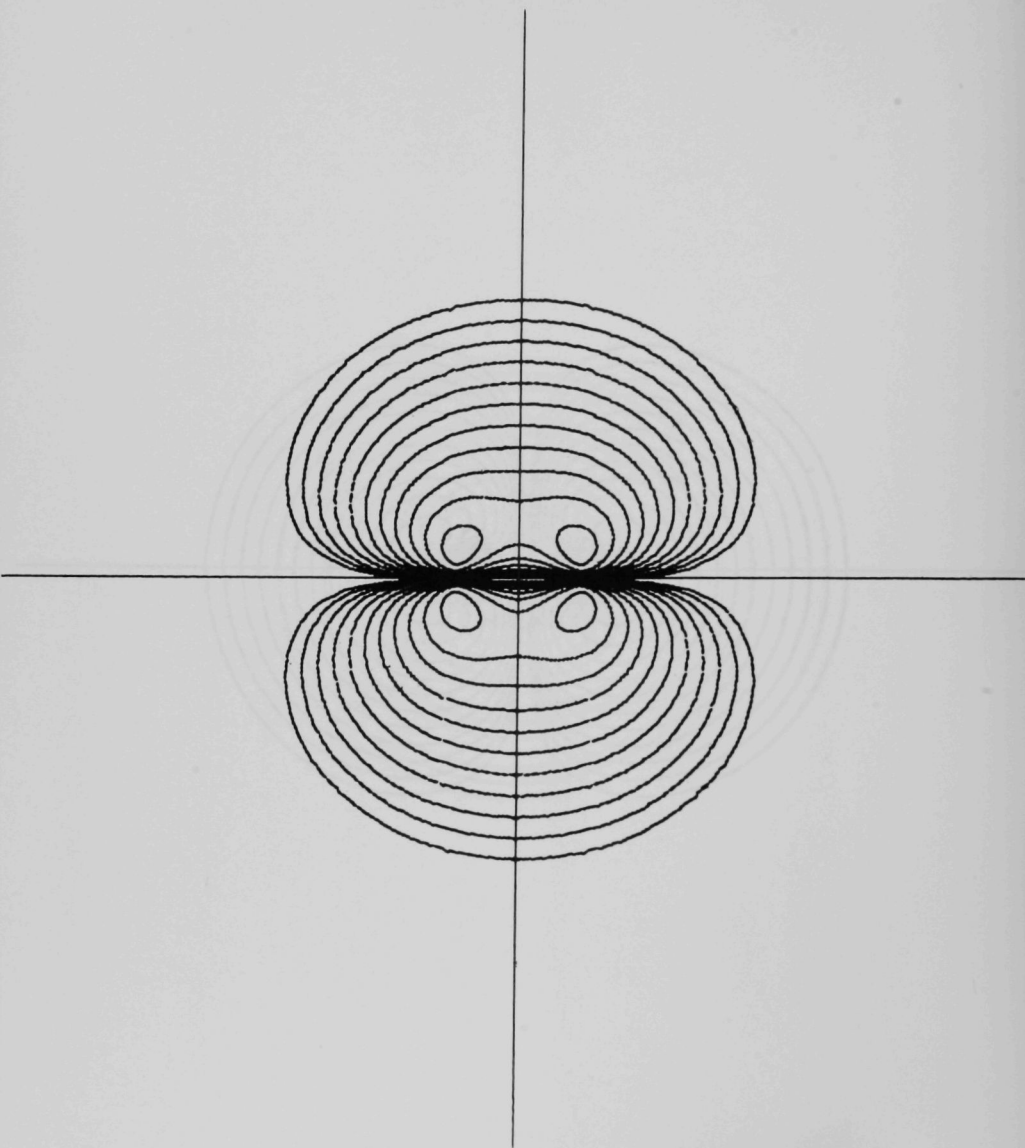


Fig. 18. Carbon $1\pi_u^*$ Orbital Density

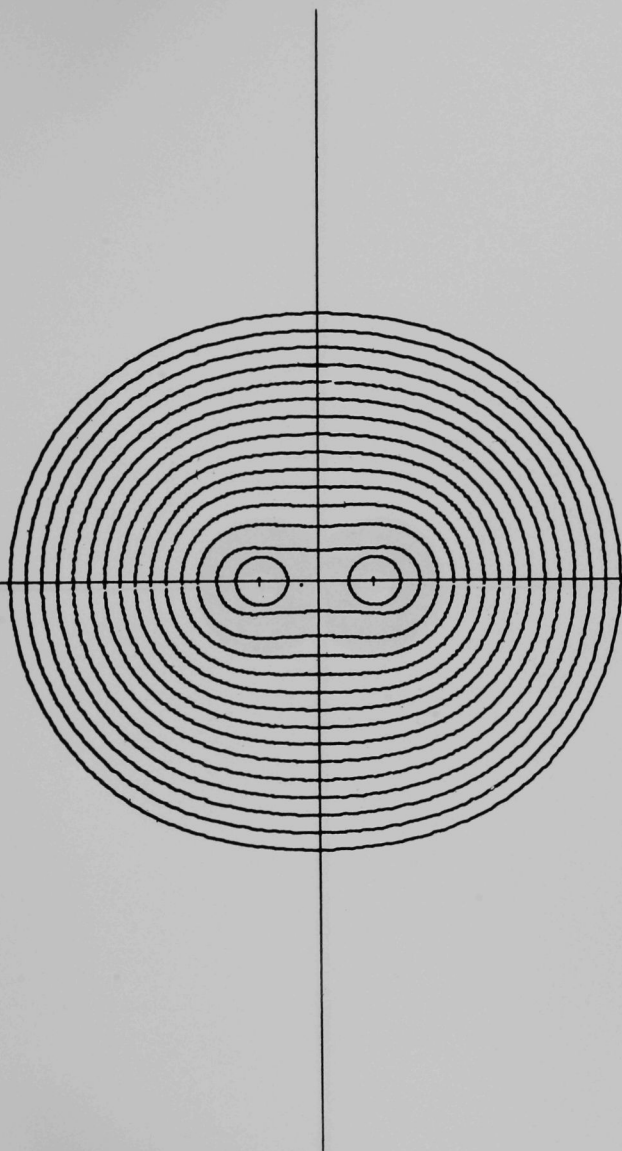


Fig. 19. Nitrogen Total Molecular Density

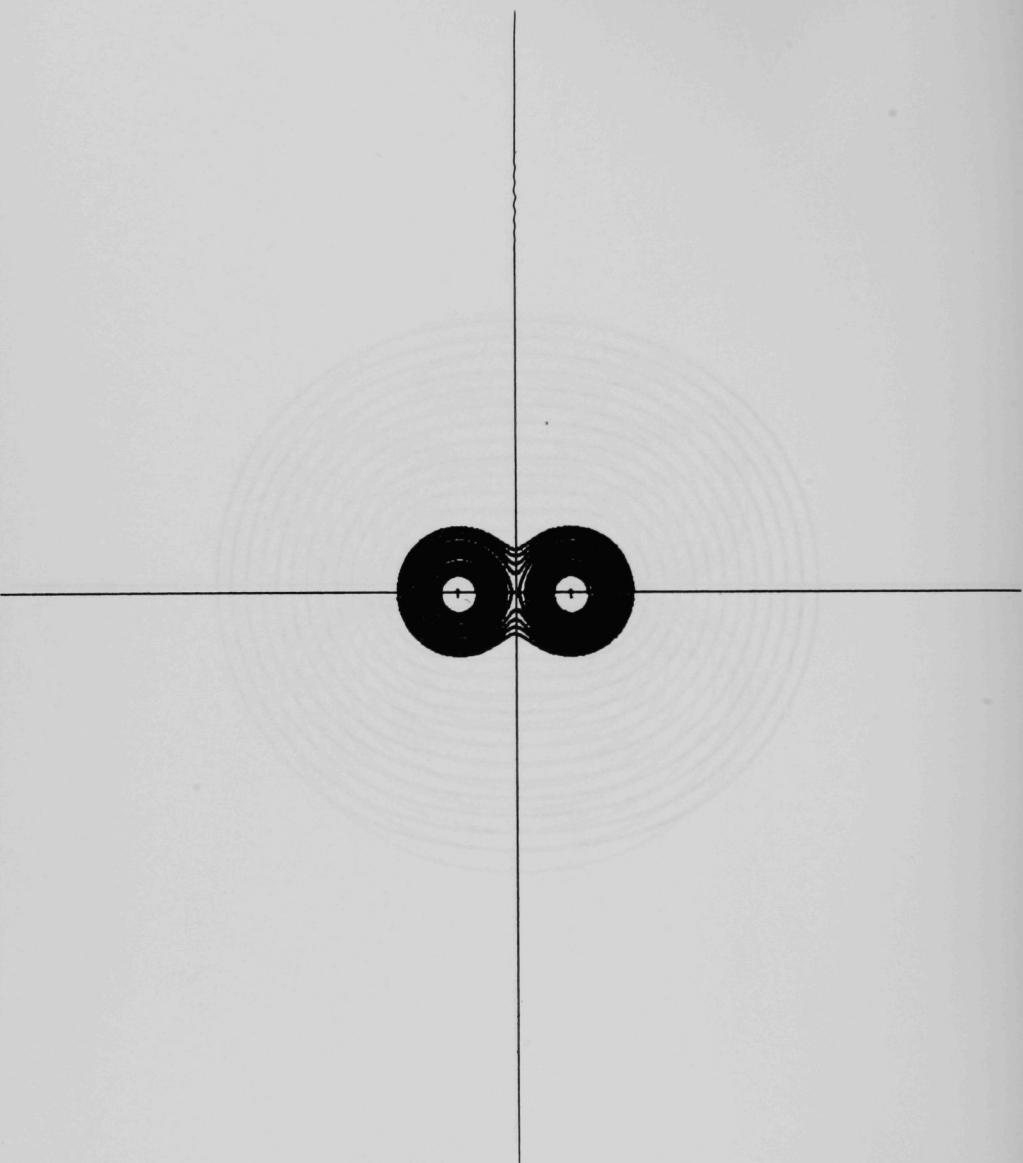


Fig. 20. Nitrogen $1\sigma_g^*$ Orbital Density

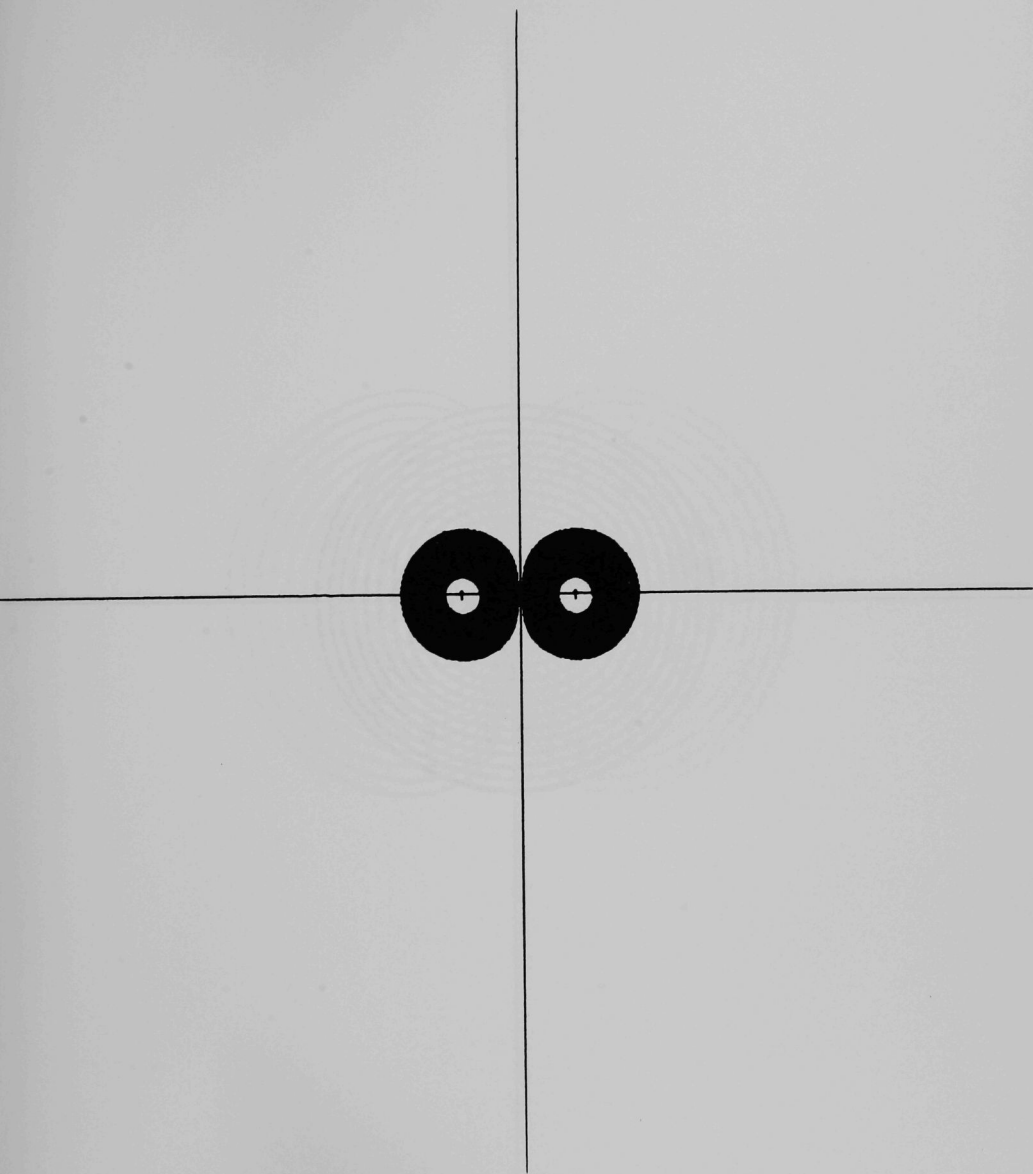


Fig. 21. Nitrogen $1\sigma_u$ Orbital Density

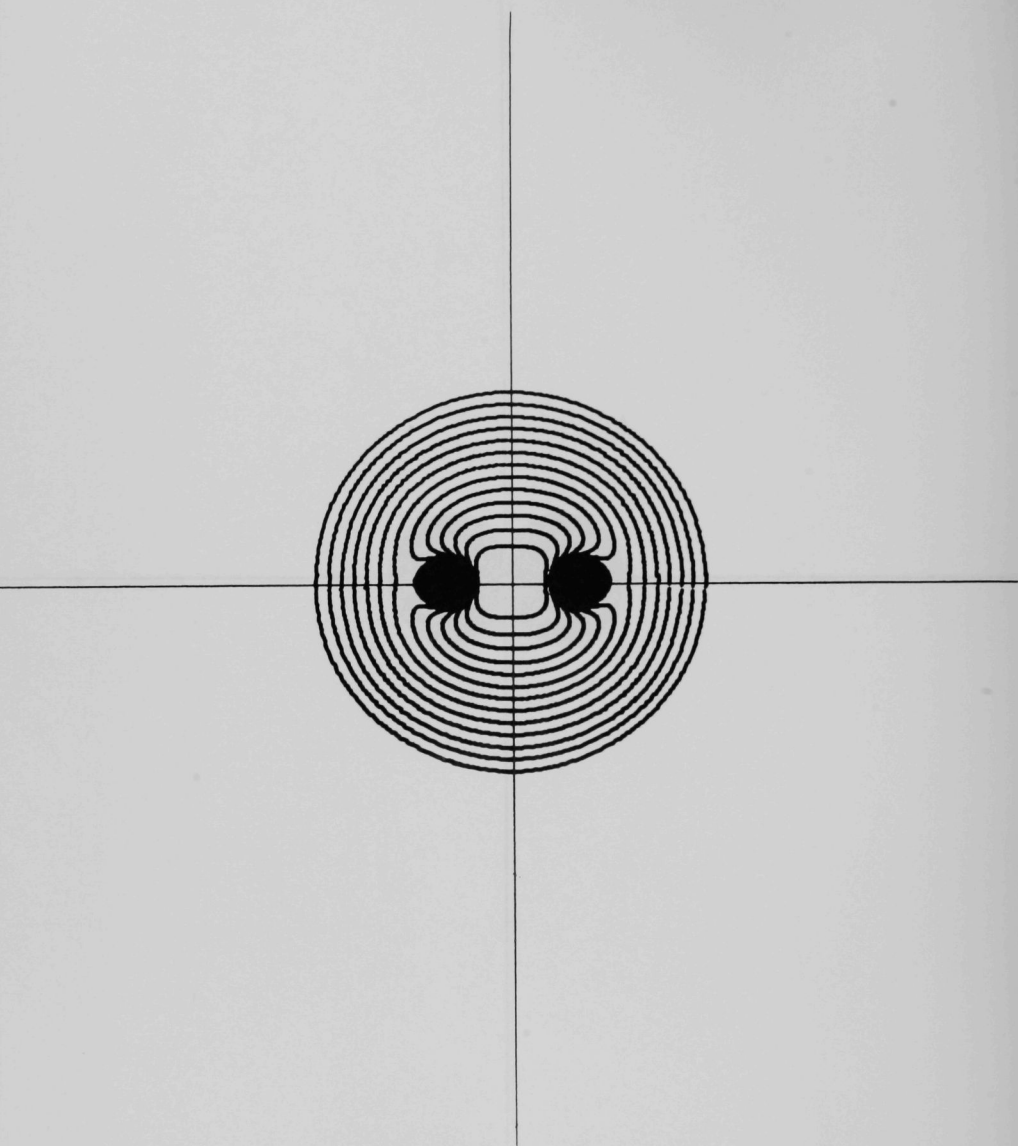


Fig. 22. Nitrogen $2\sigma_g^*$ Orbital Density

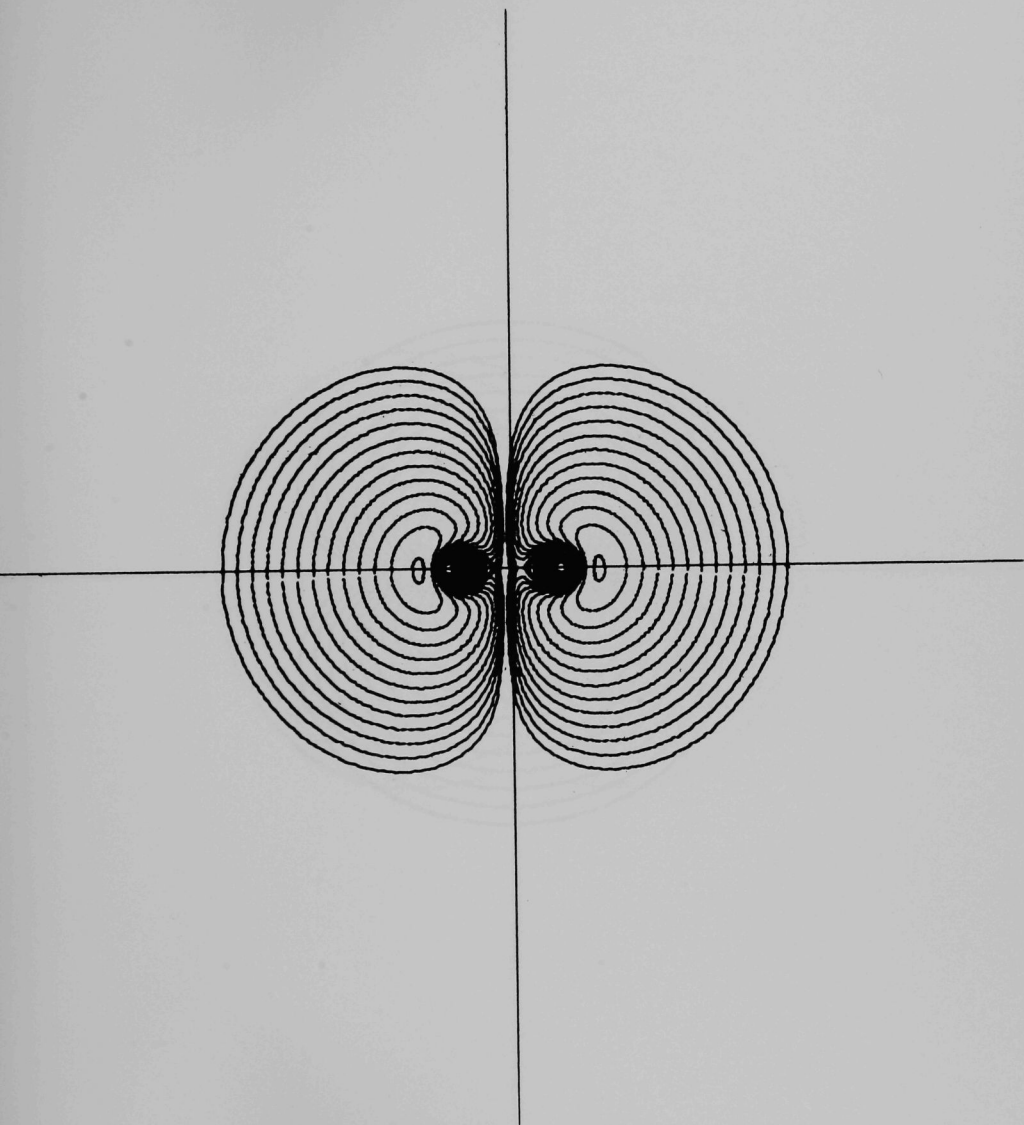


Fig. 23. Nitrogen $2\sigma_u$ Orbital Density

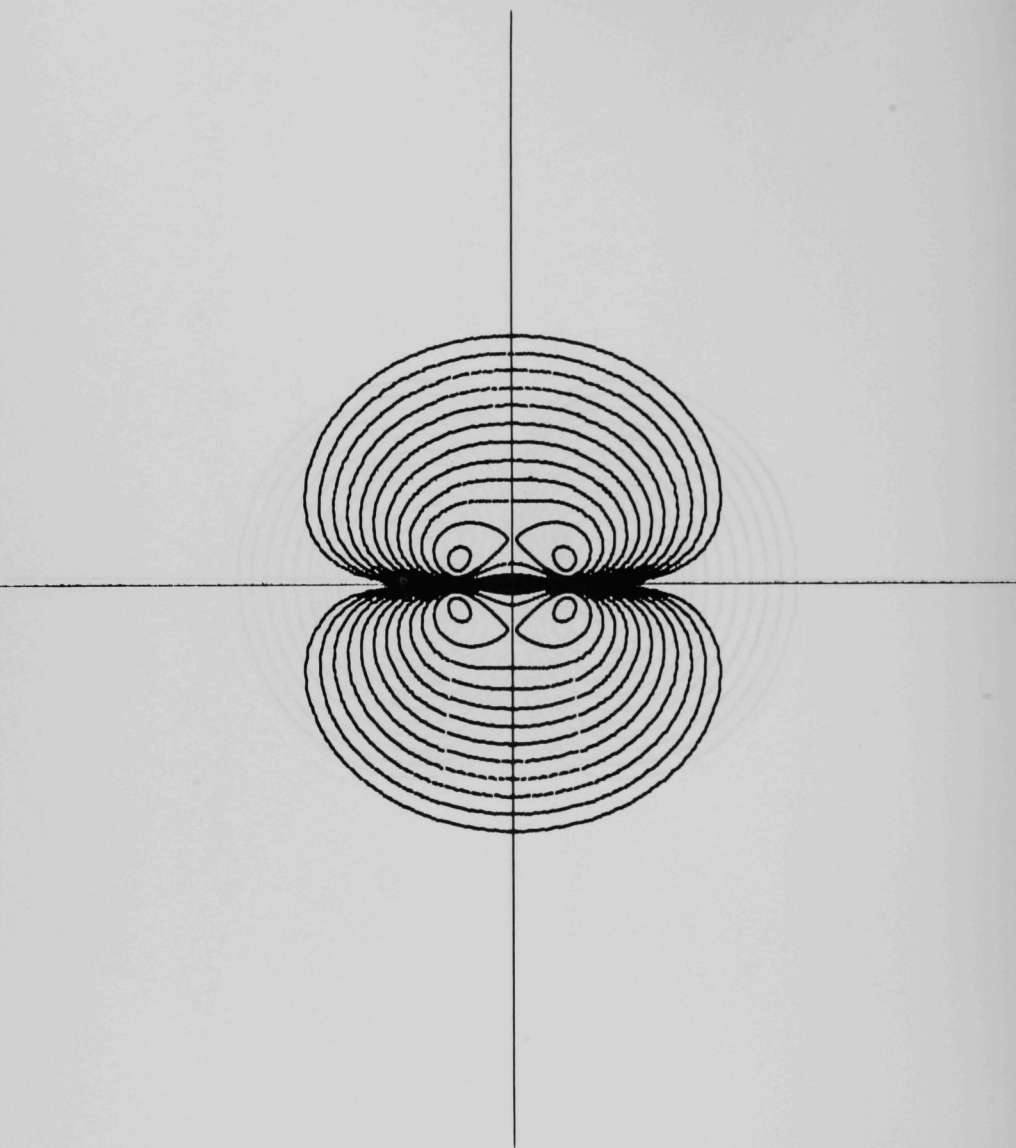


Fig. 24. Nitrogen $1\pi_u^*$ Orbital Density

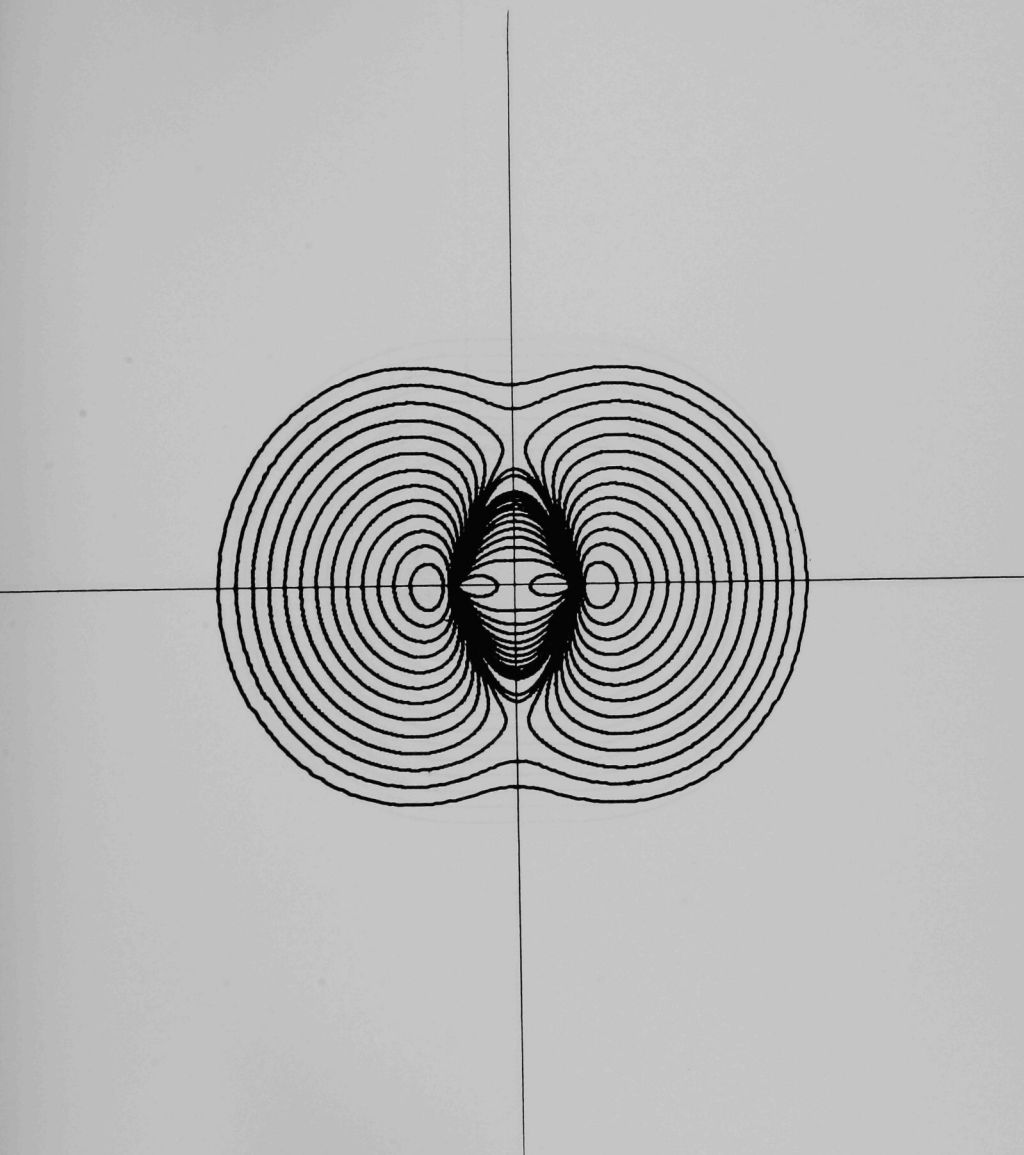


Fig. 25. Nitrogen $3\sigma_g$ Orbital Density

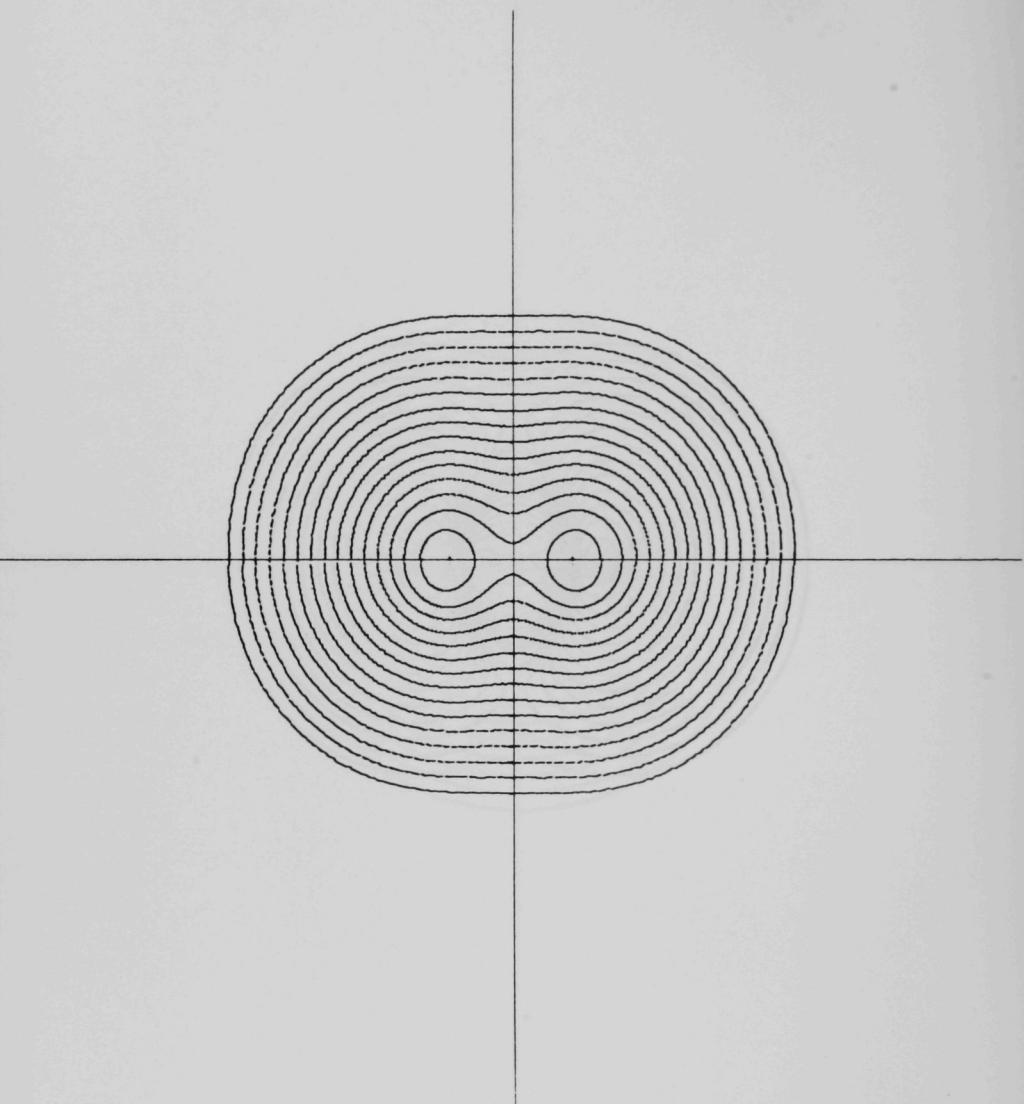


Fig. 26. Oxygen Total Molecular Density

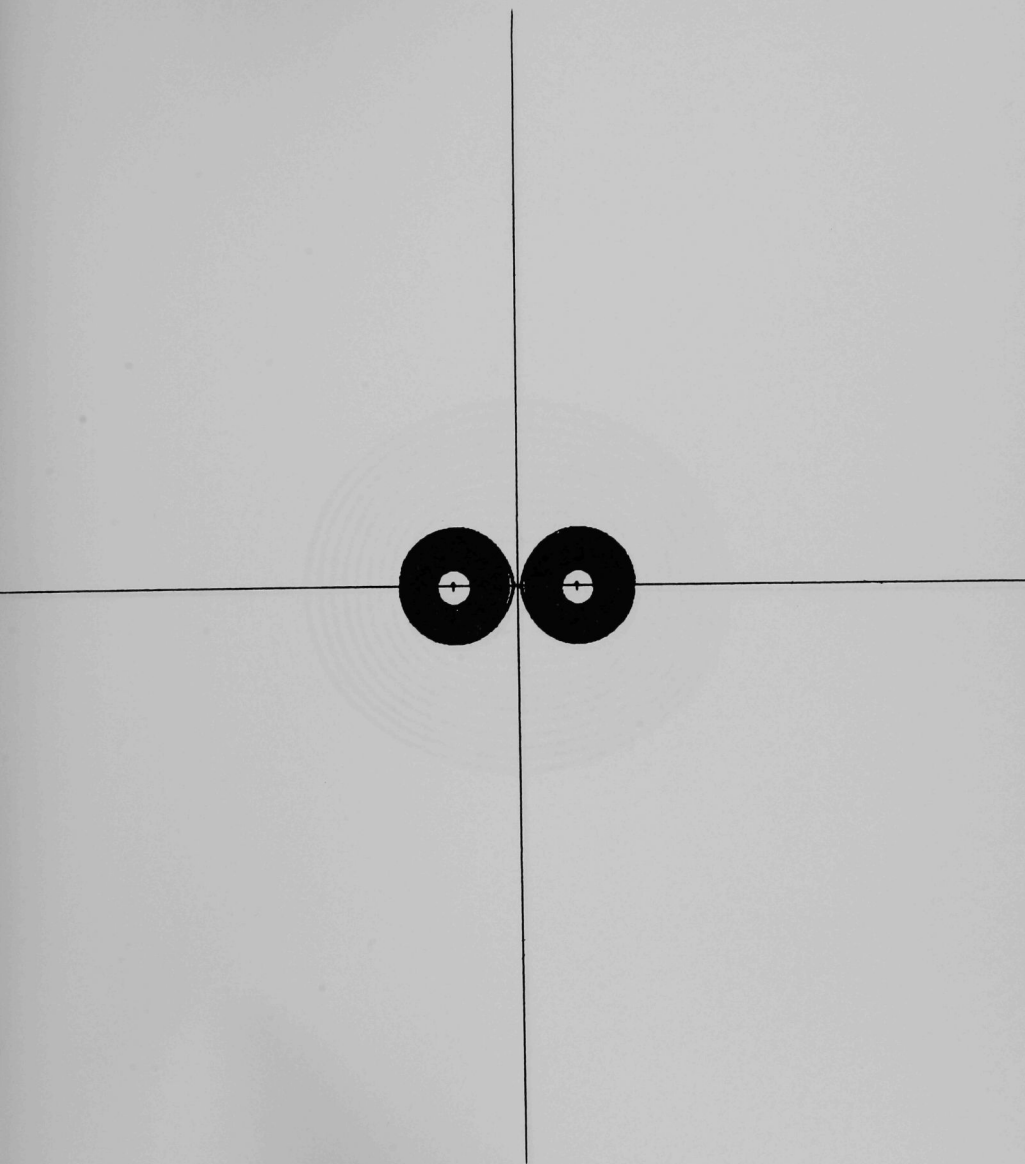


Fig. 27. Oxygen $1\sigma_g$ Orbital Density

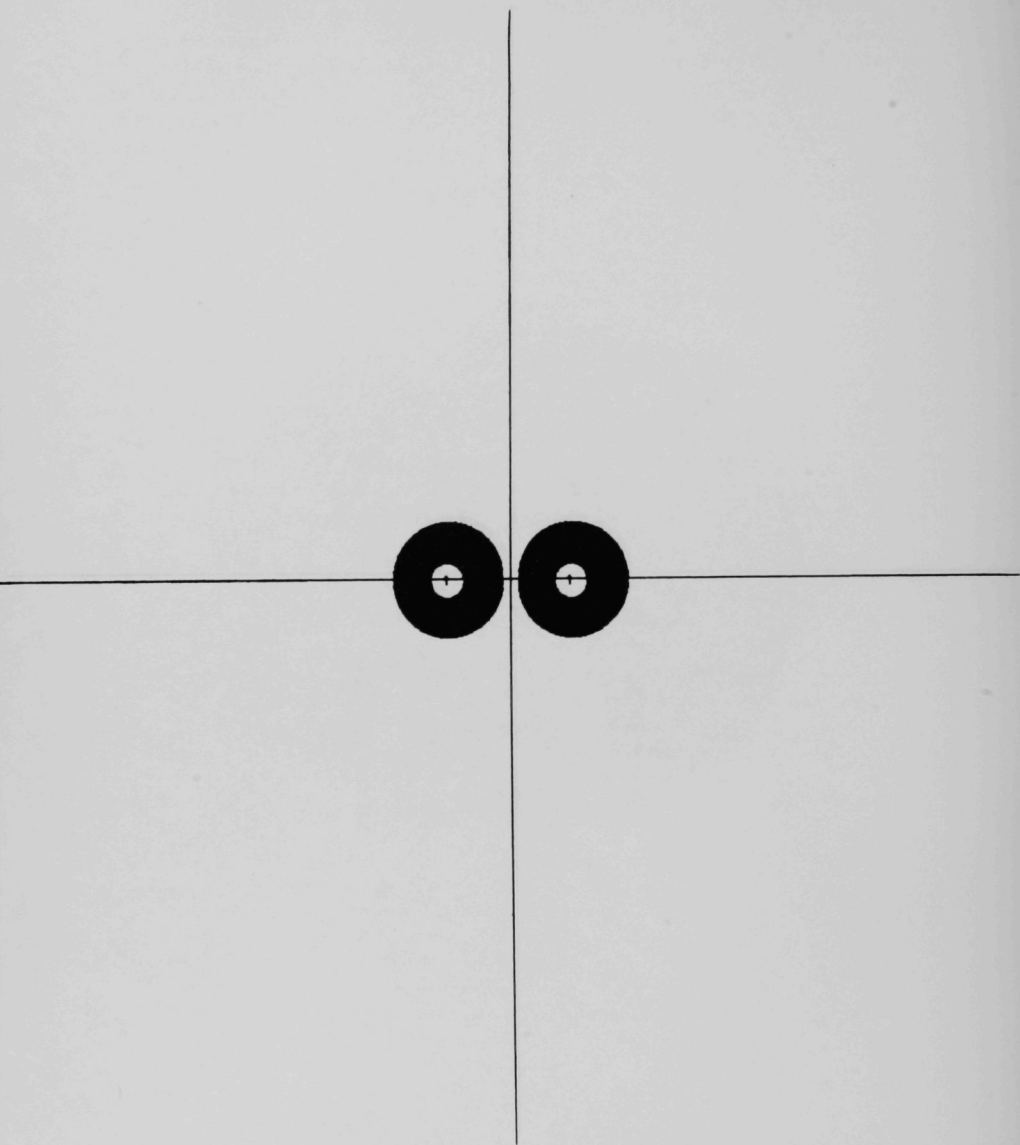


Fig. 28. Oxygen $1\sigma_u$ Orbital Density

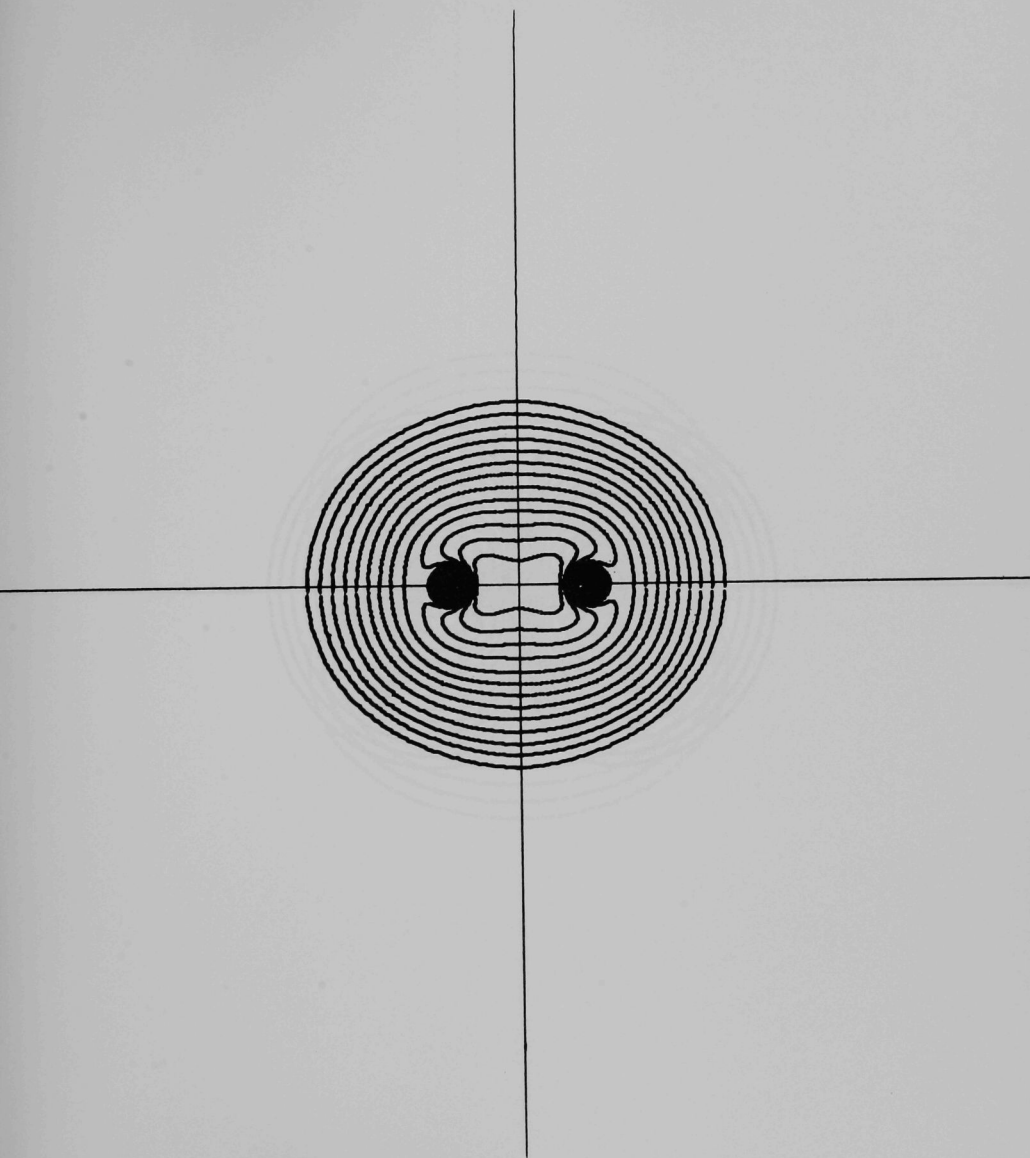


Fig. 29. Oxygen $2\sigma_g$ Orbital Density

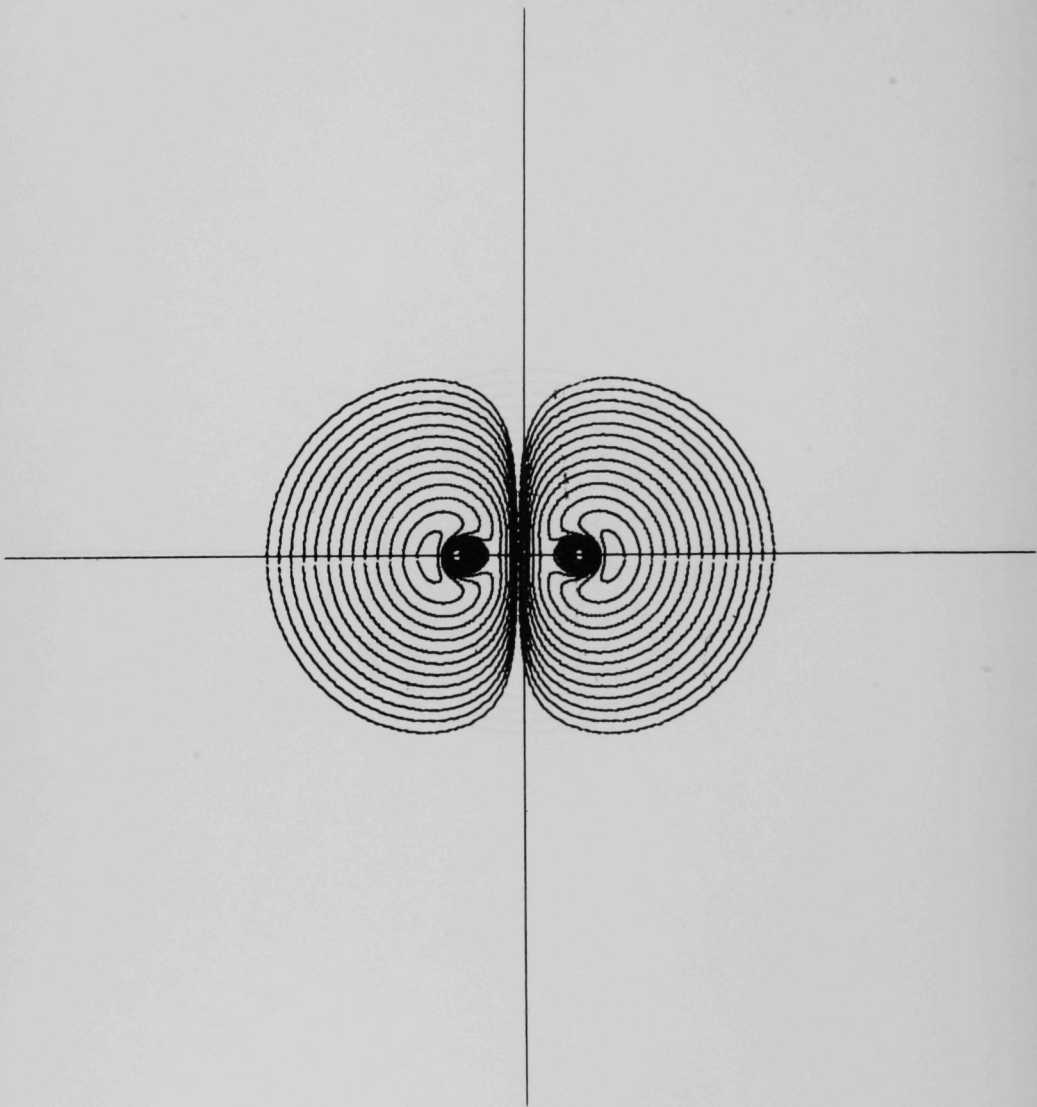


Fig. 30. Oxygen $2\sigma_u^*$ Orbital Density

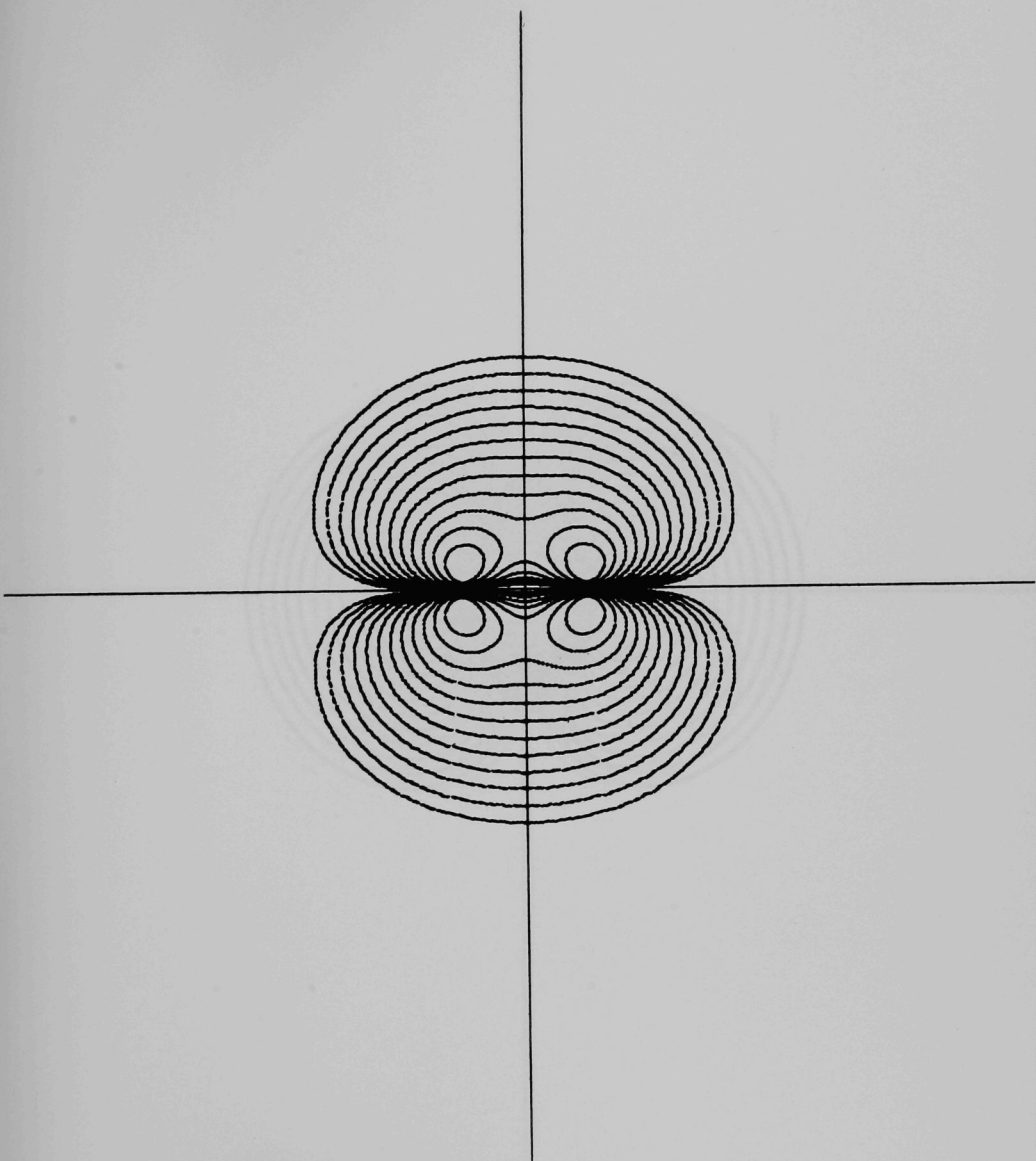


Fig. 31. Oxygen $1\pi_u$ Orbital Density

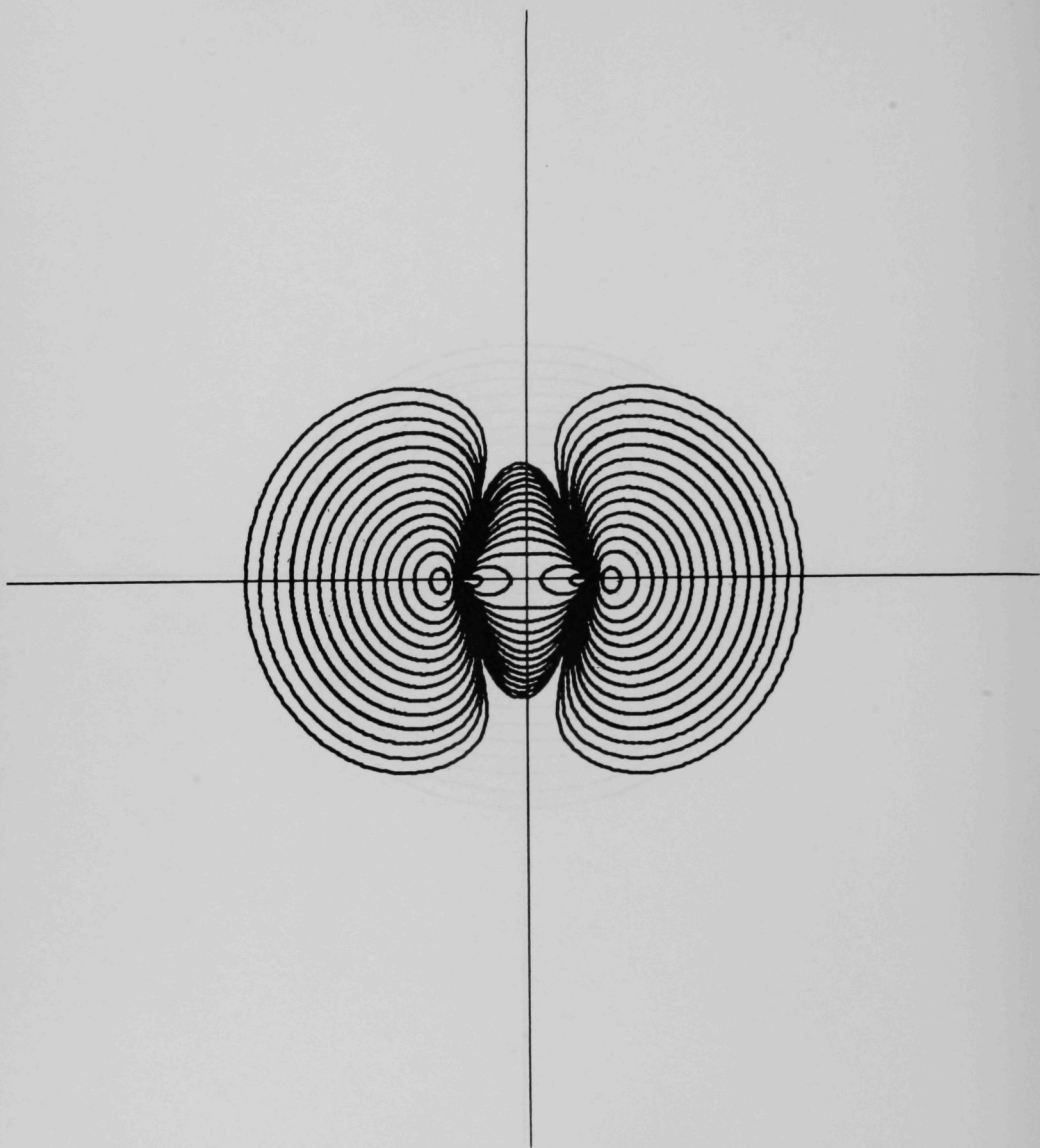


Fig. 32. Oxygen $3\sigma_g^*$ Orbital Density

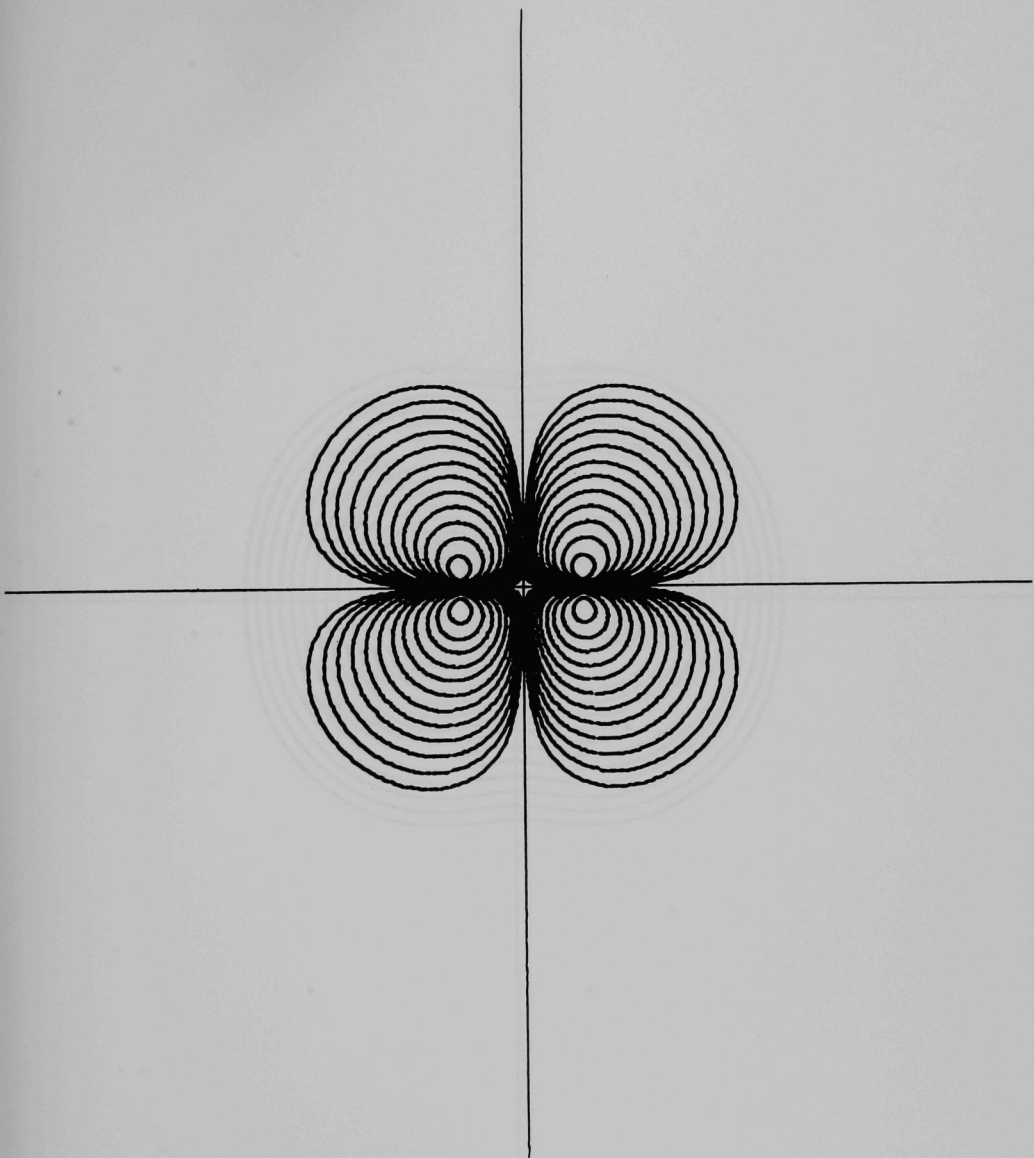


Fig. 33. Oxygen $1\pi_g$ Orbital Density

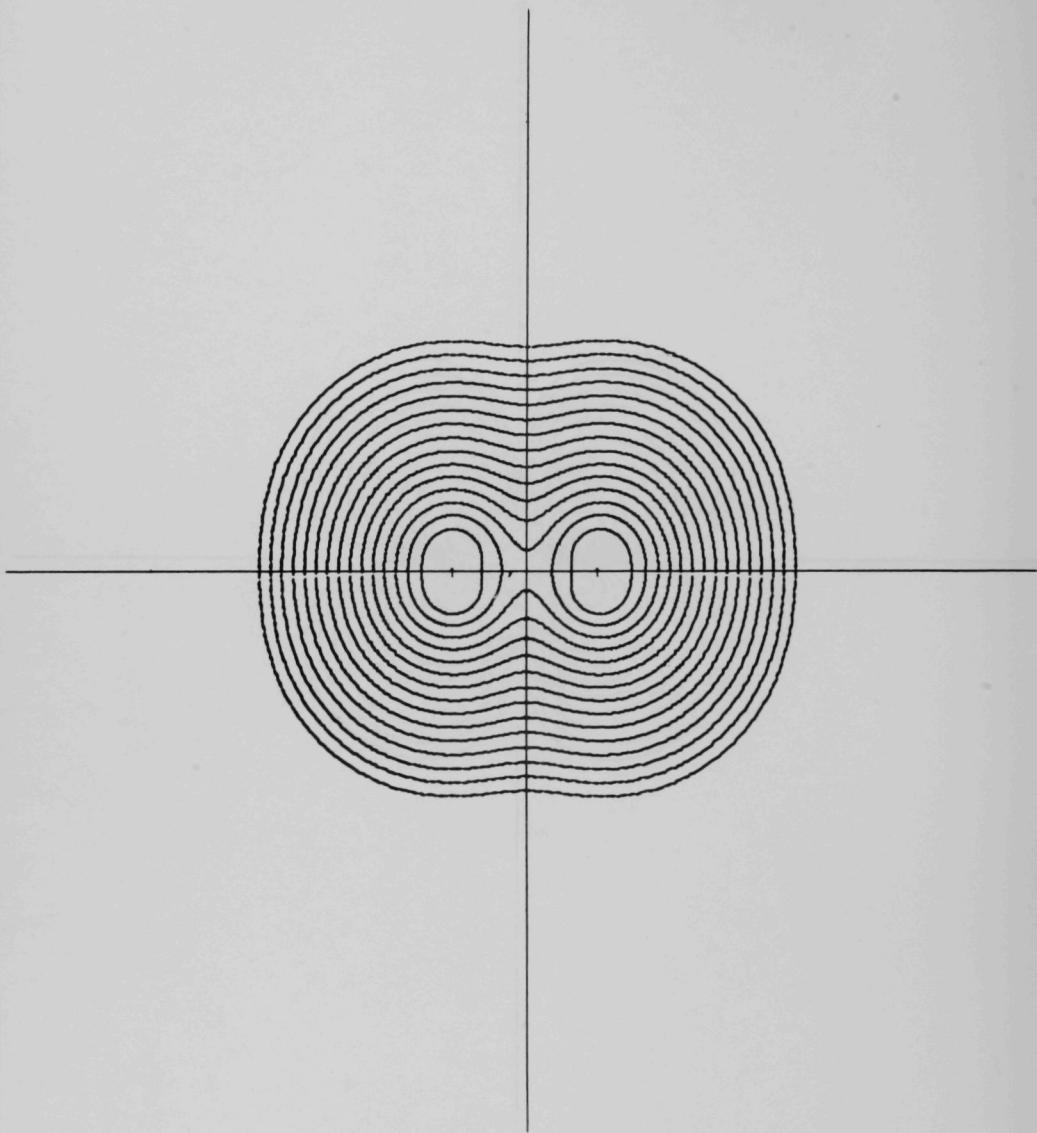


Fig. 34. Fluorine Total Molecular Density

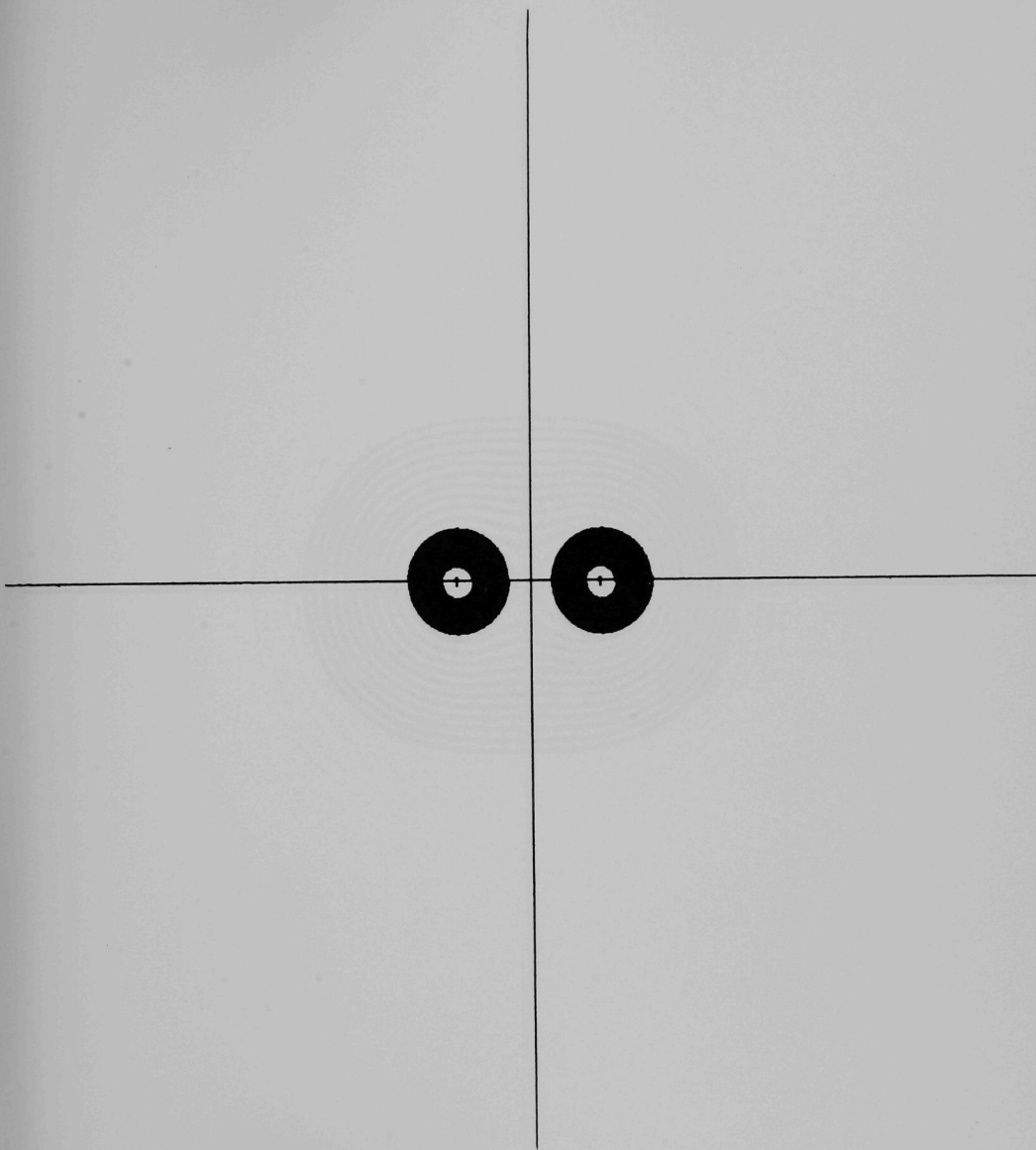


Fig. 35. Fluorine $1\sigma_g$ Orbital Density

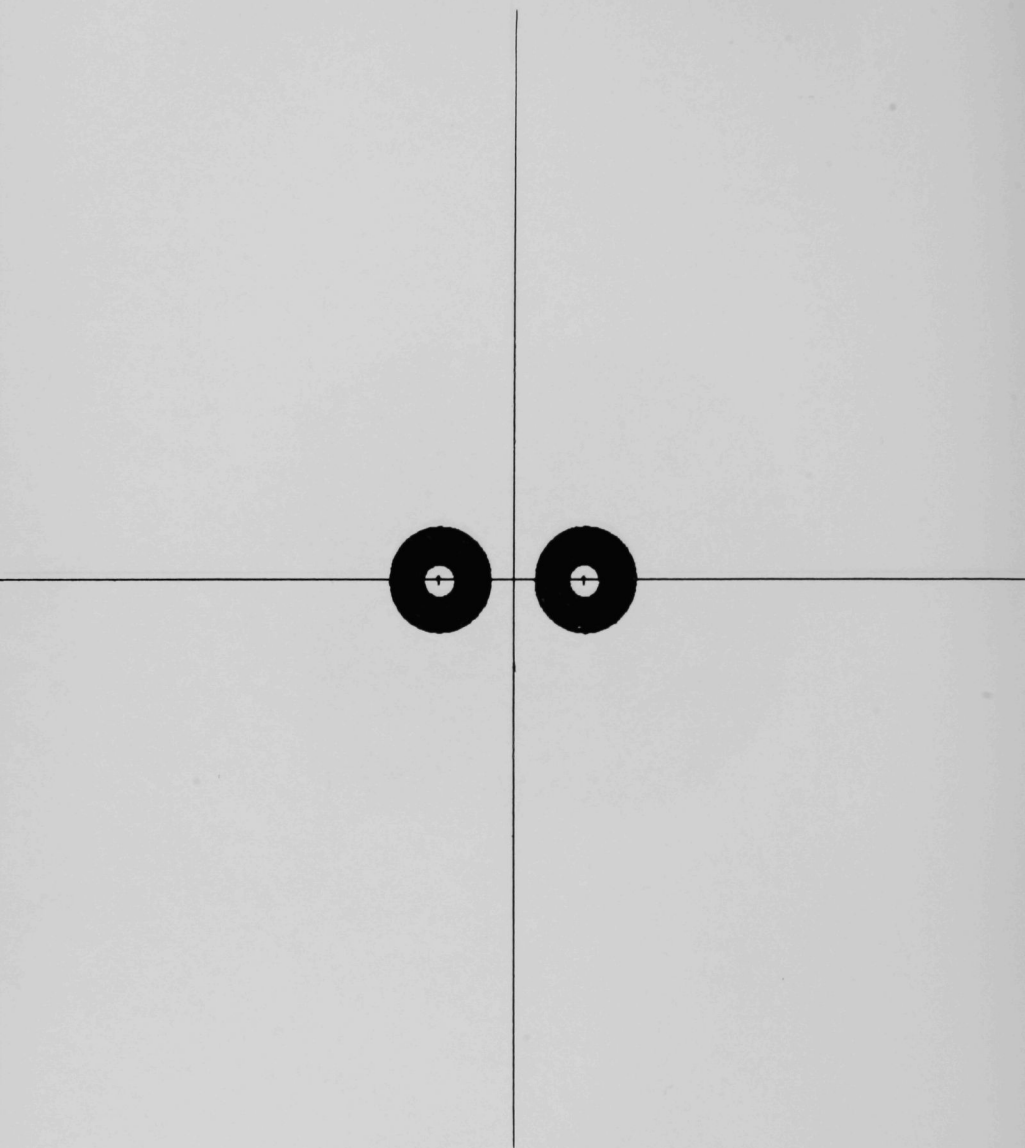


Fig. 36. Fluorine $1\sigma_u^*$ Orbital Density

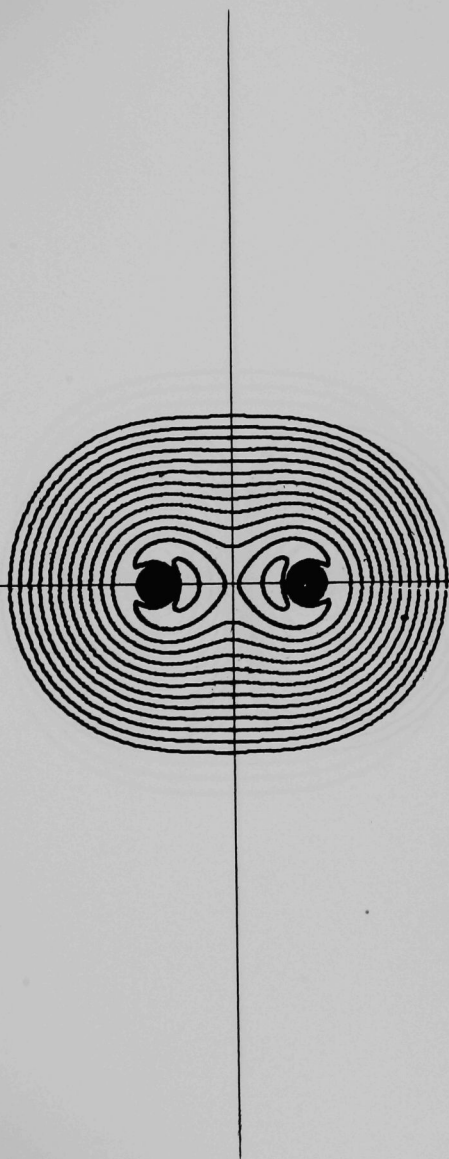


Fig. 37. Fluorine $2\sigma_g$ Orbital Density

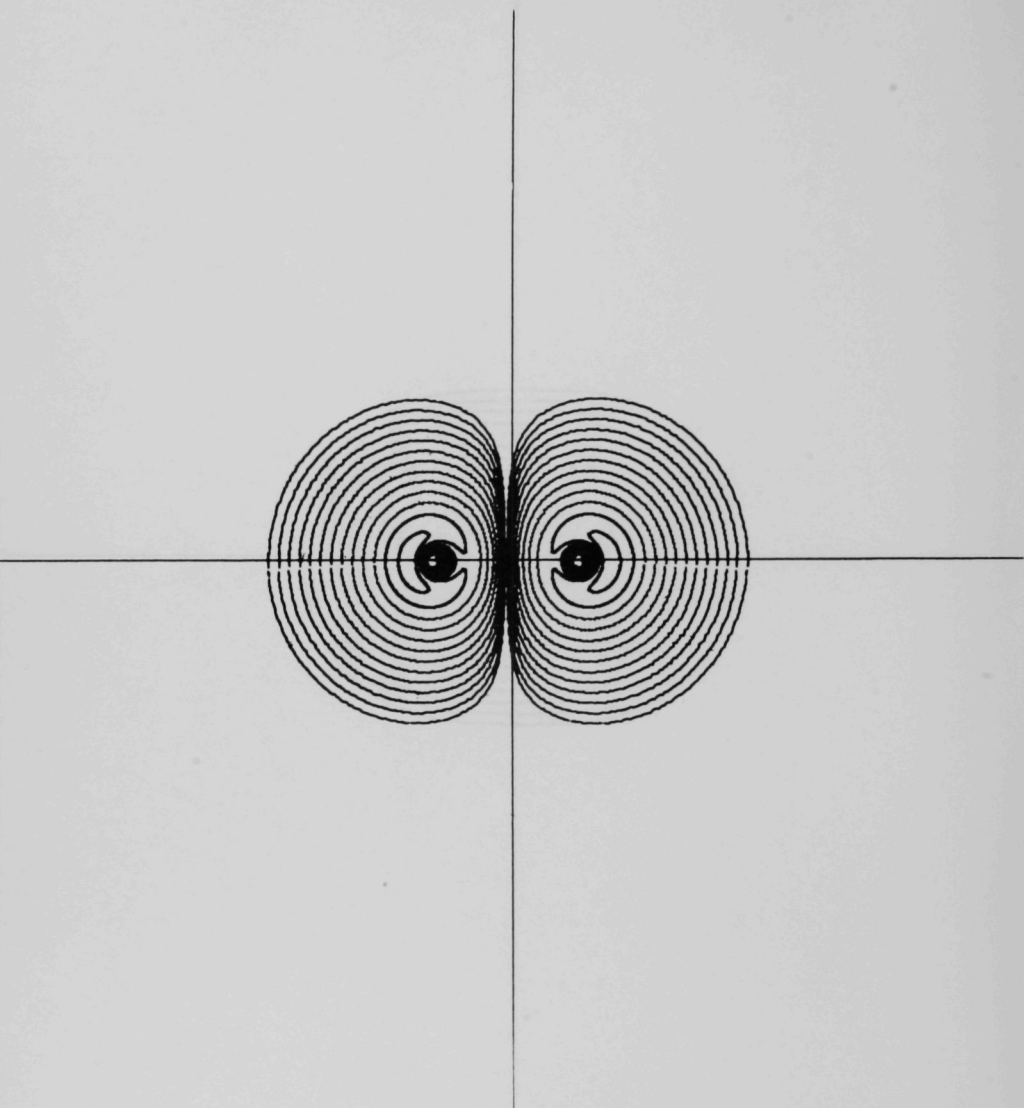


Fig. 38. Fluorine $2\sigma_u^*$ Orbital Density

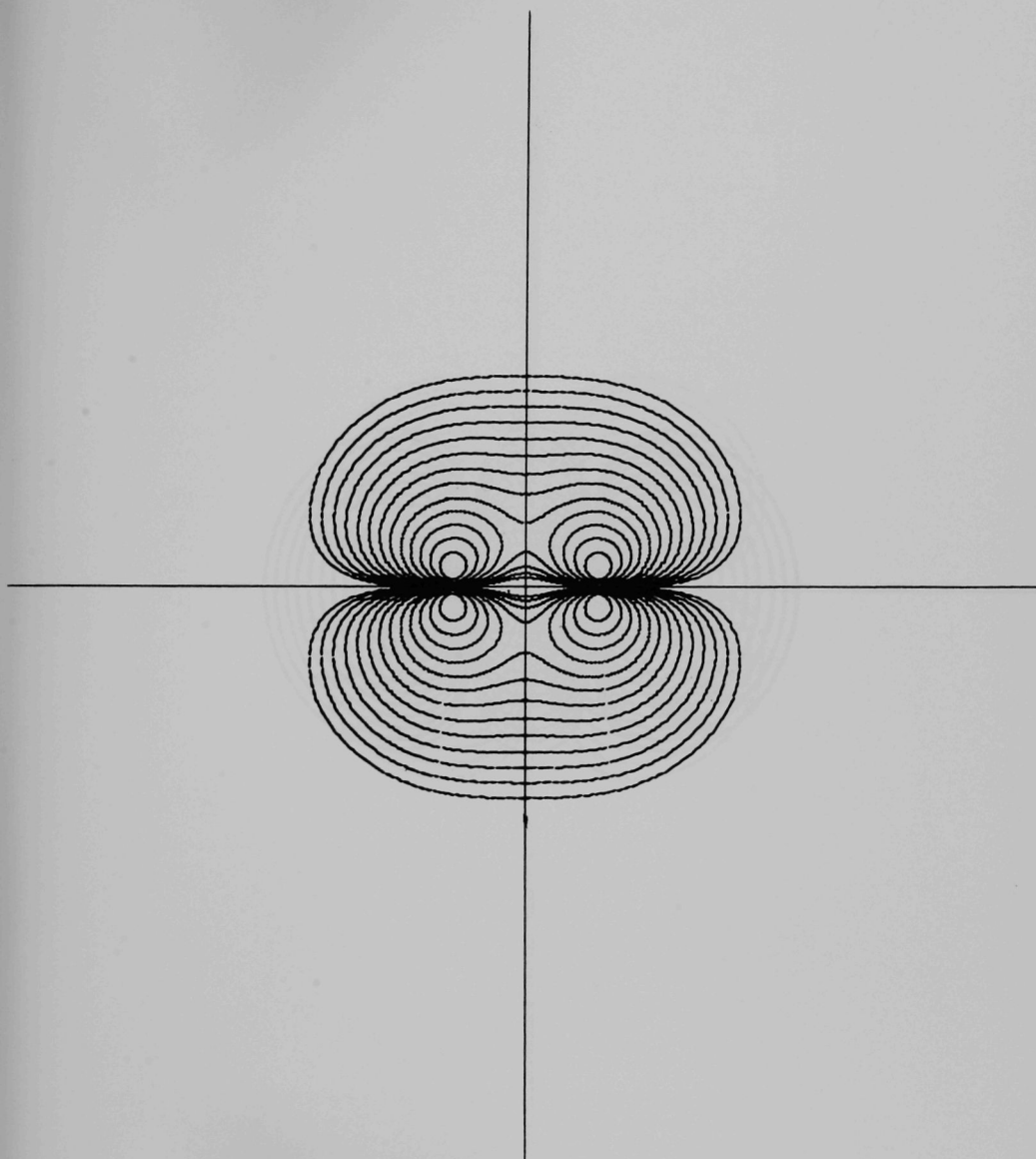


Fig. 39. Fluorine $1\pi_u$ Orbital Density

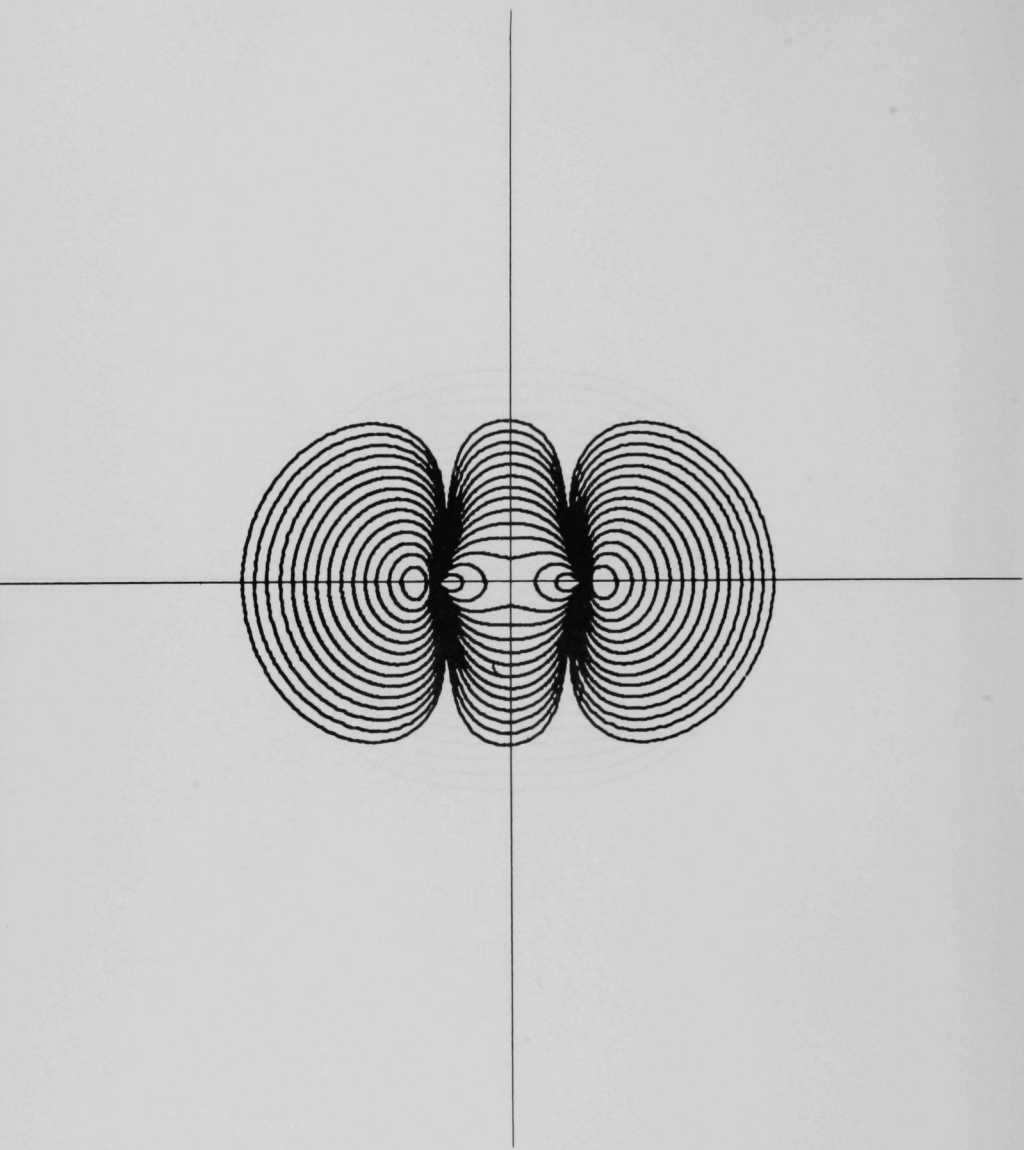


Fig. 40. Fluorine $3\sigma_g^*$ Orbital Density

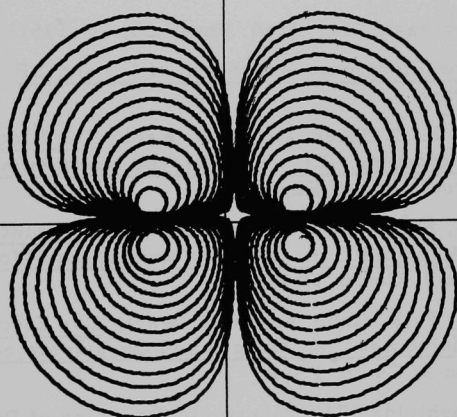


Fig. 41. Fluorine $1\pi_g$ Orbital Density

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13. S. Peyerimhoff, *Hartree-Fock-Roothaan Wave Functions, Potential Curves, and Charge Density Contours for $\text{HeH}^+(\text{X}^1\Sigma^+)$ and $\text{NeH}^+(\text{X}^1\Sigma^+)$ Molecule Ions*, submitted to *J. Chem. Phys.*
14. The wavefunctions used in this study are available from the author on request. The F_2 function is given in Ref. (2). Others will appear soon with the studies of each individual molecule. All of the functions used are thought to be very near the Hartree-Fock wavefunction of each system. The Hartree-Fock charge distribution has been shown to be a representation of the exact charge distribution to first order by Brillouin [*Actualites sci. et ind.* No. 71 (1933); *ibid.* No. 159 (1934)].

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